

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

New specific heat apparatus. ERIC GRIFFITHS. *Proc. Phys. Soc. London* 33, 355-61(1921).—An app. is described for the detn. of the sp. heats of materials such as cork, charcoal, etc., which are difficult to deal with by the ordinary methods. The calorimeter is a closed cylinder rotating on a horizontal axis. The heating coil and the thermo-elements project into the calorimeter and are maintained stationary. The material under test fills about $\frac{1}{3}$ of the calorimeter and is mixed by being carried round by fins attached to the internal surface. To insure equalization of the temp. the material is ground fine before the test. By reducing the wts. of all parts to a minimum a calorimeter of 4 l. capacity has been constructed whose water equiv. is less than 100 g. The jacket surrounding the calorimeter is made of copper wound with a heating coil. During an expt. the temp. of this jacket is maintained equal to that of the calorimeter, thus eliminating the corrections for heat loss by radiation and convection. The sp. heats of charcoal, slag-wool, diatomaceous earth, granulated cork, and baked cork (slab) at a mean temp. of 25° were found to be 0.29, 0.17, 0.23, 0.43 and 0.43, resp., and the moisture contents were 6.89%, 0.02%, 2.09% and 3.45%, resp. (that of baked cork was not detd.).

C. C. VAN VOORHIS

A convenient apparatus for the preparation of small quantities of pure nitrogen or carbon monoxide. H. P. WARAN. University of Cambridge. *Phil. Mag.* 42, 248-9(1921).—A simple app. of glass is described for the generation of N_2 by dropping Br water into dil. NH_4OH according to the formula $8NH_4 + 3Br_2 = N_2 + 6NH_4Br$. The app. consists of a glass-stoppered dropping funnel with a ground-glass stopper which is sealed into a vertical glass cylinder in the bottom of which NH_4OH stands in connection with an H tube having as its other vertical arm a glass reservoir with glass stopper and below the H arm a stopcock for filling or discharging. The N_2 is delivered from the top of the generator through two stopcocks with a reservoir contg. P_2O_5 between them. The same app. can be employed for the generation of CO by dropping concd. H_2SO_4 into formic acid, according to: $H_2CO_2 + H_2SO_4 = (H_2O + H_2SO_4) + CO$, as well as for any other gas that can be generated under similar conditions. S. C. LIND

A simple device for making crystal-structure models. K. SPANGENBERG. *Centr. Mineral. Geol.* 1921, 229-33.—Iron rods 4 mm. in diam. and 80 cm. long are attached to individual iron bases. Wooden balls of various colors are accurately bored to the same diam. They may be slid on these rods and will retain their position by friction. Assembling these rods in various ways and placing the balls in their proper position enables one to build up any point system easily and quickly. OTTO VON SCHLICHTEN

The "Hermetisator." G. SCHNEIDER. Dessau. *Chem. Ztg.* 45, 892(1921).—Instead of using an air-pump to exhaust vessels in which foods, etc., are to be preserved under vacuum a higher vacuum is more easily obtained by filling the "hermetisator" with H_2O and pumping out the H_2O . Made by Winkler & Co., Dessau. J. H. M.

A simple apparatus for preparing distilled water with constant addition of pre-heated water. O. LÄCHER. Kottbus. *Chem. Ztg.* 45, 892(1921); 1 cut.—A Cu or Sn steam generator of about 2 l. capacity, with glass H_2O gage, is connected to a vertical bulb

condenser. The warm H_2O from the condenser passes through a short rubber tube to 1 arm of a Y, the other arm carrying an overflow tube with screw cock. The stem of the Y connects to the top of the steam generator, a short glass stem with ground cock being inserted in the tubing. By adjusting the glass and screw cocks the generator is fed with H_2O as fast as it is evapd.

J. H. MOORE

Suggestions for calibrating base metal thermocouples by the freezing-point method. KIRTLAND MARSH. New Kensington, Pa. *Chem. Met. Eng.* 24, 1071(1921).—The paper deals with the protecting tube. Fe can be coated with graphite by heating to 900° and quickly plunging into a wash of 1 vol. graphite to 2 vols. water, withdrawing before the tube has lost the heat desirable for drying the coating. Finely powdered, not flake graphite must be used; it must be stirred immediately before use. The coating can be cleaned, and so used in different metals. The coated tube is more robust than refractories and contaminates the metal less than iron, or than glass does in an Al bath. In melting Cu the graphite must be protected from oxidation by an outer layer of lime, similarly applied from a 1:1 wash.

W. P. WHITE

Setting a recording pyrometer for cold-junction temperature. KIRTLAND MARSH. New Kensington, Pa. *Chem. Met. Eng.* 24, 1152(1921).—In the case where the galvanometer scale does not come down to the cold-junction temp., the pointer is set for any convenient low temp., A, then, by an adjustable small e. m. f., is deflected by an amt. $A - C$, where C is the cold-junction temp., and then set to A while the small e. m. f. continues to be applied. On open circuit the pointer, though off scale, now reads C, which is the necessary adjustment.

W. P. WHITE

The open mercury manometer read by displacement interferometry. CARL BARUS. *Proc. Nat. Acad. Sci.* 7, 71-5(1921).—The app. is essentially a U-tube, with wide shanks, cut in a rectangular block, preferably of iron. Thin plane parallel glass plates floating on Hg, which fills the U-tube, act as mirrors for the interferometer beams. A range of pressure measurement of 3×10^{-4} to 3×10^{-1} cm. of Hg is possible. Expts. are described or suggested for using the apparatus as a vacuum gage, air thermometer, abs. electrometer, etc.

H. M. McLAUGHLIN

Testing of thermometers. ANON. Bur. Standards, *Circ.* No. 8, 3d Ed.(1921).—"This Circular is designed to give such information as is useful to those who wish to send thermometers to this Bureau for test."

W. P. WHITE

Twenty-five years of liquid air (SCHREBER) 2.

Analytical balance. W. M. PESTEL. U. S. 1,387,998, Aug. 16. The pat. relates particularly to structural features of the rider beam and the device for operating it from outside the balance case.

Gas washers. W. H. GEESMAN. U. S. 1,388,812-13, Aug. 23. The gas is brought into contact with a cascade of H_2O .

2—GENERAL AND PHYSICAL CHEMISTRY

W. B. HENDERSON AND EDWARD MACK

Recent advances in science—Physical chemistry. W. B. GARNER. Univ. London. *Sci. Progress* 16, 100-5(1921); cf. *C. A.* 15, 3233. JOSEPH S. HERBURN

The teaching of chemistry in colleges and universities. GEO. W. MUEHLEMANN. *Chem. Bull. (Chicago)* 8, 176-7, 193-4, 202, 218-9(1921).

Chemistry in the Dutch Indies. A. J. KLUVVER. *Chem. Weekblad* 18, 661-7(1921).

Gabriel Lippmann. EDMOND BOUTY. *Ann. phys.* 16, 156-64(1921).

Dr. William Prout's hypothesis. EDWARD FARRELL. *Chem. Zeit.* 43, 757-8(1921).—Historical. D. MACRAE

A revision of the atomic weight of cadmium. V. The electrolytic determination of cadmium in cadmium sulfate. GREGORY PAUL BAXTER AND CARL HENRY WILSON. *J. Am. Chem. Soc.* 43, 1230-41(1921).—Hydrated CdSO₄ is not particularly suited for exact work owing to the danger of included mother liquor; and anhydrous sulfate is difficult to prep. owing to its decompr. at high temps. CdBr₂, which is rapidly freed from impurities by crystn., was converted to the nitrate by HNO₃ and then to the sulfate by H₂SO₄. The sulfate was then recrystd. Analysis of the hydrated salt by deposition of Cd in pure mercury gave 112.03 as the atomic wt., a result obviously too low. This is attributed to the presence of water included in the crystals. Anhydrous CdSO₄ was prep'd. by dehydrating the crystals at 700° in dry air which had been passed through fuming H₂SO₄. The atomic wt. detd. with this material gave values varying between 112.392 and 112.429 (av. 112.409) for the best results. JAMES M. BELL

A revision of the atomic weight of zinc. II. The electrolytic determination of zinc in zinc chloride. G. P. BAXTER AND J. H. HODGES. *J. Am. Chem. Soc.* 43, 1242-51 (1921).—Anhydrous ZnCl₂ was prep'd. by dehydrating ZnBr₂ and converting the bromide to chloride in a current of dry Cl. An aq. soln. of this salt was electrolyzed; the Zn was deposited in a Hg cathode. The atomic wt. of Zn calcd. from 11 analyses varied between 65.341 and 65.407, with a mean of 65.372. After rejection of 4 results which were considered not as accurate as the others, the av. was 65.379. This agrees closely with the result (65.376) of Richards and Rogers (*Proc. Am. Acad.* 31, 158(1895)) and the result (65.388) of Baxter and Gross (*C. A.* 10, 1122). JAMES M. BELL

Electrochemical conceptions of valency. JOHN A. N. FRIEND. Municipal Tech. School, Birmingham. *J. Chem. Soc.* 119, 1040-47(1921).—In an earlier paper (*C. A.* 2, 1518) F. postulated residual or latent valencies which are called out in pairs of equal and opposite sign, and which differ from "ionized valencies" of such compds. as NaCl. The former valencies were postulated to account for mols. composed of atoms of similar electrochem. behavior. Several difficulties with the theory are cleared up by Thomson's physical theory of valence (*C. A.* 15, 1651). Thus for K₂PtCl₆ the Cl atoms lie at the corners of an octahedron enclosing the Pt atom, such a shell being stable because the Cl atoms are joined by non-ionized valencies and the field of force due to the charged Pt atoms enhances the stability of the non-ionized Cl valencies. JAMES M. BELL

Ion mobilities, ion conductances, and the effect of viscosity on the conductances of certain salts. DUNCAN A. MACINNIES. *J. Am. Chem. Soc.* 43, 1217-26(1921).—At present there is no way of distinguishing between variations in equiv. conductance due to (a) changes in number of ions and (b) changes in mobility of ions. The alkali halides at low concn. fulfil the condition of complete dissociation; additivity of the conductance at each concn. except as this property is modified by changing viscosity. Changes of equiv. conductance may, therefore, be attributed to changes in ion mobilities arising conceivably from increasing strength with concn. of the elec. field due to the ions. The change in ion mobility is also shown by the change in transference number with concn., a change which indicates that the mobility of one or both ions is not const. J. M. B.

Cation volumes in permutite. GÖNTHER-SCHULZ. *Z. physik* 5, 324-30(1921).—G. finds the mol. vols. of salts of the form M₂O·Al₂O₃·SiO₄·5H₂O. Salts contg. only one metal (M) cannot be prep'd. by double decompr., but the mol. vol. for a mixed salt is found to be linear in the fraction of one component. Mol. vols. with 21 bases are thus found by extrapolation. Assuming at. vol. and ion vol. to be the same for the lowest at. wt.; ion vols. for these bases are computed. Of the various recent estimates of these quantities for the alkali metals, G.'s results are in good agreement only with those of Lorenz from the mobilities in Hg (*C. A.* 15, 1440). F. C. HOYT

Deduction of the dissociation equilibrium from the theory of quanta and a calculation of the chemical constant based on this. P. EHRENFEST AND V. TEKAL. *Ann. Physik* 65, 609-28(1921).—See *C. A.* 15, 790. E. H.

Twenty-five years of liquid air. K. SCHREBER. *Chem. App.* 8, 73-8, 101-4, 109-11, 120-2, 125-6, 127-8(1921); 25 cuts.—The paper includes a brief review of the early history of the techn. liquefaction of air with cuts of Cailletet's and Pictet's app., the principles of the Linde process, the sepn. of liquid air into its constituents with cuts of the app., app. for the production of liquid O₂, a table showing the % compn. of the liquid and gaseous portions between -182° (the b. p. of O₂) and -194° (the h. p. of liquid air), the Claude and Heylandt processes, a cut showing the arrangement of a liquefying plant as built by the Sirth Machine Co., Cologne, a short account of attempts to use liquid O₂ in explosives, and cuts showing a type of container for liquid air.

J. H. MOORE

Methods for the production and measurement of high vacua. Final installment. Temperature drop, slip, and concentration drop in gases at low pressures. SAUL DUSHMAN. *Gen. Elec. Rev.* 24, 890-900(1921); cf. *C. A.* 15, 3024.—A detailed review. An appendix contains tables, formulas and data which ought to prove useful in connection with investigations at low pressures. C. G. F.

The absorption of gas in a vacuum tube. F. H. NEWMAN. University College. *Beams* 9, 251-4(1921); cf. *C. A.* 15, 2027.—A short review. C. G. F.

The sorption of hydrogen by amorphous palladium. JAMES BRIERLY FIRTH. University College, Nottingham. *J. Chem. Soc.* 119, 1120-26(1921).—The author's summary is: (1) The sorptive capacity of Pd black varies according to the method of prepn. (2) Pd black contains both amorphous and cryst. Pd, the proportion of each varying with the conditions under which it was originally prepnd. (3) The sorptive capacity of Pd black at low temps. depends on the temp. at which sorption begins. (4) Pd black satd. with H at 100° sorbs further quantities of H when gradually cooled in the gas. (5) A comparison of the sorptive capacity at definite temps. varying from 100° to -190° shows a slight decrease from 100° to 20° and a continuous increase from 20° to -190°. (6) When Pd black is heated, the proportion of the cryst. variety increases. JAMES M. BELL

The sorption of alcohol and water by animal charcoal. JOHN DRIVER AND JAMES B. FIRTH. University College, Nottingham. *J. Chem. Soc.* 119, 1126-31(1921).—The rate of sorption of water (from water vapor) by charcoal is exceedingly slow, requiring about 70 days to attain equil. (0.13 cc. per g. of C); for alc., equil. is reached in about 37 days (0.62 cc. per g. C). For alc.-water mixts., alc. is preferentially sorbed and equil. is reached more rapidly with mixts. higher in alc. Langmuir's theory (*C. A.* 11, 2849) that such are capillary phenomena is disputed on the ground that this theory would require the absorptive capacity of charcoal to be about the same for all liquids. This conclusion is not in accord with the facts. JAMES M. BELL

Negative adsorption of alkali haloids by wood charcoal. ALWYN PICKLES. *J. Chem. Soc.* 119, 1278-80(1921).—Measurements have been made of the adsorption by wood charcoal of NH₄Br, NH₄Cl, LiCl, KBr, KCl, KI, NaBr and NaCl from aq. solns. at a number of temps. between 10 and 100°. Birch charcoal in a very fine state of division was employed. This charcoal had been prepnd. during the war for use in the newer types of gas masks. It was found that, in the presence of charcoal, solns. of the above named salts all first showed a slight decrease and then, with the exception of LiCl, a continuous increase in concn. with rise in temp. This decrease is attributed to a diminishing surface effect; but as the temp. increases the solvent opens up the complex interior of the charcoal by dissolving the oxidation products, blocking the ends of the capillaries. H. JERMAIN CREIGHTON

The theory of gels. III. S. C. BRADFORD. *Biochem. J.* 15, 553-62(1921); cf. *C. A.* 13, 1411; 14, 1919.—Further evidence is adduced that the reversible sol-gel transformation of the natural emulsoids is an extreme case of crystn. and soln. B. H.

Autodiffusion in solid lead. J. GRÖH AND G. V. HEVASSY. *Ann. Physik* 65, 216-22; cf. *C. A.* 15, 334.—The autodiffusion in solid Pb was detd. by measuring the rate of flow of a radioactive Pb into inert Pb at room temp. and at 280°, 40° below its m. p. The rate was found to be less than 10^{-4} cm². per day, a value less than $\frac{1}{100}$ the rate of diffusion of Au into solid Pb according to Roberts-Austen (*Trans. Roy. Soc. London* 187, 404(1896)). Expts. with Ra D, a homolog of Te, gave only negative results indicating that all metals are not so active in this regard as Au. F. O. A.

Solutions saturated with two or more solutes. Application of LeChatelier's principle. C. RAVRAU. *Compt. rend.* 172, 1089-1102(1921).—The law of reciprocity is stated thus: Let a soln. be satd. with *A* (but without excess of solid *A*) and be almost satd. with *B*. Now add *B* to satn. If now more *A* be added and if more pass into soln., the addition of *B* augments the solv. of *A*. Reciprocity requires that addition of *A* will also increase the solv. of *B*. Diminution of solv. is also reciprocal. This statement is shown to accord with several cases but does not agree with results for $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$. R. believes that a redetn. of the data would bring this case under the rule. JAMES M. BELL

Ion properties and crystallochemical affinity. I. The properties of the ions in crystals. H. GRIMM. Munich. *Z. physik. Chem.* 98, 353-94(1921).—The electrostatic action or the "field-action" in crystals is traceable to (a) the charge of the ions, (b) the radius of the ions, and (c) the structure of the ions, particularly to their surface (to the number of outer electrons). The following principal types of ions are differentiated according to the number of outer electrons: (1) ions of the He type with 2 outer electrons, (2) ions of the inert-gas type with 8 outer electrons, (3) ions of the Cu^+ , Ag^+ , Au^+ type with probably 18 outer electrons, (4) ions of the type of Tl^+ and Pb^{++} , transition ions of the type Mn^{++} , Fe^{++} , Co^{++} and Ni^{++} . For many physical properties it has been found that $\phi_A - \phi_B > \phi_X - \phi_Y > \phi_K - \phi_L$, where ϕ is the numerical value of the physical property. This inequality is traced back to an analogous irregularity which holds for the radii of ions. The ionic radii of O^{--} , S^{--} , Se^{--} , Te^{--} , Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++} have been calcd., and the radius of Cs^{++} has been estd. The sequence of other ionic radii has been deduced from the gradation of the mol. vol. of isomorphous compds., the interchangeable ions of which have the same number of outer electrons. Ions having both different structures and different outer shells exhibit similar "field-action" in crystals, provided the differences of the outer shells are compensated by radial differences. On plotting the at. numbers against the ionic radii, several breaks in the curve are obtained. The different parts of the curves may be extrapolated for unknown ionic radii. H. JERMAIN CREIGHTON

Theory of binary mixtures. VII. The mixture ethyl ether-bromoform. F. DOLEZALEK AND M. SCHULZE. Charlottenburg. *Z. physik. Chem.* 98, 395-429(1921); cf. *C. A.* 14, 660, 1776.—On mixing Et_2O and $CHBr_3$ a partial, mutual adding on of the components takes place, the resulting compd. contg. a mol. of each component. The compd. so formed is capable of dissoc. and undergoes decompr. with increase in temp. $CHBr_3$ is highly associated and, in accordance with the law of mass action, the degree of association decreases with decrease in the $CHBr_3$ concn. The vapor pressure of $CHBr_3$ at 25° and 75° has been measured by a statcal method. From the results obtained and the value of the association const. the mol. constitution of this substance has been deduced. At 25° pure $CHBr_3$ consists of 65% bimols.; a mixt. of 1 mol. Et_2O and 1 mol. $CHBr_3$ contains 23% of the compd. formed by the union of these substances. On mixing Et_2O and $CHBr_3$, at 25°, a very marked decrease in vol. occurs, the contraction

curve being depressed towards the CHBr_3 axis in consequence of the association of this substance. The vol. change for all concns. of the mixt. has been calcd. Measurements have been made of the thermal expansion of the mixts. and the data obtained employed to calc. the contraction at 15, 20 and 30°. Calcs. of the d. of the mixts. from the contraction show that measurement of the vol. change is the most exact method for the detn. of the d. of easily volatile mixts. It is shown that the phys.-chem. behavior of $\text{Et}_2\text{O}-\text{CHBr}_3$ mixts., in which both mol. combination and association occur, can be described from a knowledge of the combination const. and the association const., both of which can be ascertained from vapor pressure measurements at 2 concns. From these two consts. the mol. constitution can be ascertained numerically. H. J. C.

Reversibility of the reaction: $\text{CaCO}_3 \rightleftharpoons \text{CO}_2 + \text{CaO}$. PIERRE JOLIBOIS AND BOUVIER. *Compt. rend.*, 172, 1182-3 (1921).—To explain the apparent irreversibility of this reaction, where Iceland spar and ptd. CaCO_3 are dissociated by heat and the CO_2 is absorbed again only partially, it is suggested that there are solid solns. of CaO and CaCO_3 , at high temps. As the above reaction occurs at surface layers, coatings are formed which prevent a rapid attainment of equil. Where an excess of lime is present, equil. conditions are reached more rapidly. JAMES M. BELL

Interaction of oxalic acid with iodic acid. III. Influence of sunlight. GEORGES LEMOINE. *Compt. rend.*, 173, 192-7 (1921); cf. *C. A.*, 15, 975, 3017.—These expts. were carried out in direct sunlight, on clear, warm, spring or autumn days. Under these conditions the effect of the sun was const. for several hrs. The 2 N mixts. of $\text{H}_2\text{C}_2\text{O}_4$ and HIO_3 were brought to the temp. which they would acquire from the sunshine and poured into parallel-sided containers lying on red Cu which was perpendicular to the sun's rays. The rates of reaction were measured by the vol. of CO_2 evolved and by titration. The law of speed of the reaction is $d(y/p)/dt = k[1 - (y/p)]^2$, in which p is the wt. of the mixt., y is the wt. decomposed, t is the time, and k is a const., negative in this case. Calcs. based on this equation were confirmed by expt. The presence of the sunshine caused as rapid a reaction at 30° as would take place at 37° in the dark. The light was less effective after passing through a layer of the mixt. F. E. BROWN

Periodic reaction in homogeneous solution and its relation to catalysis. WILLIAM C. BRAY. *J. Am. Chem. Soc.*, 43, 1262-7 (1921).—The reactions $5\text{H}_2\text{O}_2 + \text{I}_2 = 2\text{HIO}_3 + 4\text{H}_2\text{O}$ (1), $5\text{H}_2\text{O}_2 + 2\text{HIO}_3 = 5\text{O}_2 + \text{I}_2 + 6\text{H}_2\text{O}$ (2), and $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ (3) take place in soln. Reaction 1 proceeds rapidly in a moderately high acid concn., and is markedly autocatalytic; reaction 2 proceeds slowly under most favorable conditions (low H-ion concn.); reaction 3 accompanies both of the others. For a soln. of H_2O_2 , KIO_4 , and 0.110 N H_2SO_4 , the vol. of O_2 shows a steady increase with time, after an induction period of 7 min. For a soln. similar except that the H_2SO_4 was 0.055 N the rate of evolution of O_2 was slower after 60 min. than in the first expt. after 7 min. For two solns. of intermediate acid concn., 0.073 and 0.0918 N with H_2SO_4 , the evolution of O_2 was a periodic phenomenon. This is evidence in favor of the intermediate reaction theory of catalysis. This seems to be the first instance of a periodic reaction in homogeneous soln. In a soln. so arranged that oxygen is evolved so slowly as not to cause bubbles the I color could be seen to deepen and fade periodically; so the periodicity cannot be due to the periodic release of oxygen. It has also been shown that light, traces of a chloride and the presence of a suspended solid have a marked influence on the reactions. F. E. B.

Adsorption of gases by metallic catalysts. H. S. TAYLOR AND R. M. BUNN. *J. Am. Chem. Soc.*, 43, 1273-87 (1921).—Measurements of the adsorption of H_2 , CO , CO_2 and C_2H_4 by finely divided Ni, Co, Fe, Cu, Pd and Pt were made. Adsorption by a metallic catalyst is not like adsorption by such inert substances as charcoal and silica gel. It is specific and satn. capacity is reached at low partial pressures of the gas. It is a surface phenomenon involving electronic rearrangements in both catalyst and adsorbed gas.

Methods of prepn. which produce good metallic catalysts also produce metals with high powers of adsorption for gases whose reaction they catalyze. But the temp. of max. absorption is often lower than temp. of max. chem. activity. This probably means that a free evapn. of both reactants and resultants is necessary for rapid chemical action. The greater the adsorption the lower is the temp. at which catalytic action begins. F. E. B.

Variations in the catalytic power of electroplatinosols caused by stabilizers. A. de GREGORIO ROCASOLANO. *Compt. rend.* 173, 234-6(1921); cf. *C. A.* 15, 3018.—Electroplatinosols were stabilized at successive times by Na lysalbate, by Na protalbate, by gum arabic, and by gelatin. In each case the catalytic power of the sol was decreased by the presence of the stabilizer. With small amts. of stabilizer the decrease of catalytic power depends on the amt. of stabilizer present but as larger amts. are added each unit has less effect until a point is reached at which added stabilizer does not affect the catalytic power sensibly. From this R. concludes that catalytic power resides in chem. compn. and not in the colloidal condition. In fact the stabilizing of the colloidal condition causes a decrease in catalytic power. F. E. BROWN

Catalytic activity of copper. II. WILLIAM GEORGE PALMER. *Proc. Roy. Soc. London* 99A, 412-25(1921); cf. *C. A.* 14, 3183.—The previous investigation has been extended both by using CO and MeOH vapor as reducing agents in the prepn. of the catalyst, and by employing other alcs. for the catalytic dehydrogenation reaction. In the present expts. a continuous record has been made of the catalytic activity while the temp. of the reaction is gradually increased. The dehydrogenation of (1) EtOH in the presence of Cu prepnd. from CuO by reduction with CO and with MeOH vapor, and (2) iso-PrOH in the presence of Cu prepnd. by reduction with MeOH vapor has been studied. It has been found that the activity of the catalyst does not necessarily increase continuously as the temp. of its prepn. from the oxide is lowered. This result is reconcilable with the supposition that metallic Cu formed by the reduction of Cu₂O is the active agent. Below 270°, all the reaction-velocity-temp. curves strictly conform to the relation $v = Ae^{-K/T}$, where the symbols have their usual significance. The temp.-velocity law is interpreted by imagining that the catalytic process resembles the therm.-ionic emission of electrons from hot metals. It is shown that the catalytic activity is given by the expression $v = AB e^{-K/T} e^{aT} = AB e^{-aK}$ (where a and B are consts.), i. e., the catalytic activity is independent of temp. The presence of H₂O has been found to exert a "promoter" effect. This could be predicted from the quantum theory of radiation, since the chem. similarity of H₂O and the aliphatic alcs. would lead to similar spectra in the infra-red region. H. J. CREIGHTON

Catalysis and specifically acting catalysts: Remarks on the work of Karl W. Rosemund and F. Zetsche. E. ABEL. *Ber.* 54B, 1407-9(1921); cf. *C. A.* 15, 2435.—R. and Z. have failed to note important previous articles on the specificity of catalysts. The conclusions from their exptl. results are criticized. D. MACRAE

Statistical mechanics and chemistry. E. P. ADAMS. Princeton Univ. *J. Am. Chem. Soc.* 43, 1251-4(1921).—A mathematical paper in which it is shown that Tolman's criticism (*C. A.* 15, 459) of Marcellin's attempt (*C. A.* 9, 1710) to base theory of chem. dynamics upon the principles of statistical mechanics is unfounded. H. J. C.

Theory of imperfect gases. HEINRICH MACHE. *Z. physik* 5, 363-70(1921).—M. investigates what can be detd. by pure thermodynamics about the behavior of a gas at very low temps., on the assumption that the pressure expansion coeff. and the sp. heats have the same temp. dependence. Arguments for this assumption are drawn from the thermal relations of metals at low temp., the Nernst heat theorem and the quantum theory. M. shows that a gas, on this assumption, has always the same form for the adiabatic as an ideal monatomic gas. The equation of state will be in the form

$$p - (\dot{B}/v)\Theta = (R/v)\Theta v(T/\Theta)$$

where $\Theta = Av^{-1/2}$, A and B are pure consts., and φ is a function that must vanish at abs. zero. A probable form for φ is $1/(e(\Theta/T) - 1)$. F. C. HOFF

Simple gliding in tin and its change of condition at 161°. O. MÜCKE. Göttingen. *Centr. Mineral. Geol.* 1917, 233-9.—A study of the behavior of the twinning lamellas of Sn on heating it to its m. p. indicated that the form stable above 161° is crystallographically very similar to the tetragonal Sn of ordinary temps. Edw. P. HOLDEN

The application of the hydrogen electrode. I. M. KOLTHOFF. Utrecht. *Chem. Weekblad* 18, 468-72(1921).—K. describes what is meant by the H-ion and how it is dtd. Before going into the practical application of the H-ion he mentions some theoretical considerations, and then briefly mentions what is meant by the "P." After this K. discusses briefly the practical application of the H electrode in pure chemistry, the action of enzymes and their importance to and the organism and the importance of the H-ion in food chemistry and agricultural chemistry, as well as in bacteriology and biology.

VINCENT VERMOOTEN

Recent progress in thermo-electricity. CARL A. F. BENEDICKS. *J. Inst. Metals* 24, 7-55(1921).—A high-grade popular lecture, extended over the material presented in the papers reviewed in *C. A.* 14, 140 (especially), 2289, 2438. W. P. WHITR

New determination of the relation of the two specific heats of hydrogen by experiments with the Behn tube; and a calculation of the mechanical heat equivalent. W. RÜCKER. Marburg. *Ann. Physik* 65, 393-422(1921).—Behn's tube is a resonance tube closed at both ends. Studies of the management of such a tube with H are given. Three somewhat different series of detsns. gave results differing by 2.4 per mille. A probable error of 0.3 per mille was computed from these. The final value was $K = 1.4053$. Lummer and Pringsheim (1898) had found 1.4084, and R. considers this the most trustworthy previous value. R.'s result was based on $K = 1.4028$ for air, the mean of 11 values varying from 1.4018 to 1.4035. The value of J was computed by a thermodynamic formula calling for specific heat, compressibility and expansion data, and came within 1.7 per mille of the Reichsanstalt value. W. P. WHITR

Ruling test plates for microscopic objectives: sharpness of artificial and natural points. A. MALLOCK. *Nature* 108, 10-1(1921).—The conditions to be observed in ruling test plates for microscopic objectives are described, and tracings of photographs are shown which illustrate the relative sharpness of various artificial and natural points.

W. H. ROSS

Thermal and electric conductivity of metals (MEISSNER) 3. Optically minimal particles (SCHIRMANN) 3. Chromogenetic properties of sulfur and certain other elements (DAVIS, RIXON) 3. The periodic table (MARGARY) 3. Formation of mixed crystals by the contact of solid phases (VEGARD) 3. Viscosity of gelatin solutions (DAVIS, et al.) 29. Theory of illuminants (SCHRÖTER) 4. Color and chemical constitution (MOIR) 10.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

The part played by different countries in the development of the science of radioactivity. ROBERT W. LAWSON. *Scientia* 30, 257-70(1921). E. H.

The evolution of matter. F. W. CLARKE. *J. Wash. Acad. Sci.* 11, 289-30(1921).—C. renews the suggestion made in 1873 on spectroscopic evidence, that chem. elements were formed by a process of evolution from the simplest form of matter, that they were developed at high temps. and that when a certain stage in the cooling mass was reached, these elements combined with one another to form compds. The formation of compds. represented an advanced degree of complexity with a corresponding instability. By

this evolutionary process, in which there has been no interruption from the formation of the elements to our present chemical changes, the earth was built up. In the org. compds. this evolution has occurred until a max. complexity has been reached. In the evolution of the elements the process is slow; in the compds. it is more rapid. Thus the process of evolution becomes gradually more and more rapid. The most complex elements are unstable but stability is also detd. by symmetry, pressure, temp. and chem. environment. With a change of pressure, temp. and environment regular evolution of the elements according to atomic weights was not possible. The order was that of relative stability. In the hottest stars the most stable elements were formed. As cooling went on other elements were formed. The ten or eleven most abundant elements have atomic wts. less than 59. They are structurally the most simple and probably the most stable. This whole scheme of evolution may be thought of as a series of waves, in which the crests represent the elements and the depressions the gaps between them. These waves are highest in Fe and decrease in height as the atomic wt. is increased and instability becomes evident. In the atom the internal conditions are most important for stability. Symmetry is easiest to attain in the simpler elements. This favors their evolution. The work on the isotopes might have a different interpretation from that ordinarily given. It may be that the so-called *isotopes* are disintegration products produced by positive rays. This suggestion seems the more probable from the fact that elements of largest atomic wt. have the largest number of isotopes and should also show the greatest number of disintegration products.

A. W. SMITH

The structure of the electron. G. A. PERKINS. *Philippine J. Sci.* 181, 325-40 (1921).—The general methods of attack on the problems of the structure and properties of electrons are briefly reviewed. The fundamental problem of chemistry is to express in a quant. manner the interaction of atoms at short distances. Since atomic forces are only the aggregate of electronic forces the problem is resolved into finding the manner in which electrons and positive electric units act at short distances. The classical electromagnetic theory holds for elec. forces for all distances between those of mol. dimensions and very large ones. Without assuming some external influence quite foreign to this theory it is not possible to understand why the electron would not fly to pieces under the action of repulsive forces. There is open the other possibility of disregarding the classical theory for infinitesimal distances and inventing new laws to explain the exptl. evidence. This is a choice between an unchangeable charge and a mysterious hindering force. Whatever the ultimate nature of electrons they have apparently const. elec. charge and probably const. mass, but there is no evidence that they have const. shape under different conditions. The Lorentz electron, which is a rigid sphere, from the relativity standpoint satisfactorily represents electrons which are in uniform motion or in uniform acceleration but it is not satisfactory for an electron with non-uniform acceleration such as an electron in an atom. Electrons in atoms have magnetic effects and radioactivity teaches that even the nuclei contain electrons in extremely rapid rotation. On the classical theory these rotations would be accompanied by a steady loss of energy hy radiation. Such a loss of energy does not take place. On the other hand a rotating disk or hollow sphere or other shape with circular symmetry would give magnetic effects without radiation. Such considerations lead to the conception of a ring electron, at least to the assumption that an electron is not perfectly rigid. Assuming then a force which holds the elec. charge together the electron in a non-uniform accelerating field will be distorted in a manner similar to the tide producing distortion of the earth. These tidal motions may produce a ring electron. In the atom the electrons are in definite stable positions both inside the nucleus and outside it. Considering these electrons to be rings of electricity rotating about a positive nucleus, let there be a displacement of the positive nucleus in the plane of the ring. There is then set up a

vibrational wave in the ring. Where the circumference of the ring contains one, two, three, etc., complete wave lengths of vibrations, standing waves will be set up in the ring. Hence the vibrating ring electron seems to offer a working hypothesis for the stability and definiteness of atoms, entirely consistent with classical electrodynamic theory.

A. W. SAMSON

Ether and metether. P. LENARD. *Jahrb. Radioakt. Elektronik* 17, 307-65 (1920).—Contrary to the theory of relativity of Einstein, which avoids the term "ether," L. asserts that the phenomena which originated this theory (aberration, Michelson's expt., Fizeau's expt. and others) can just as well be explained by a theory based on a new conception of the light ether. L. distinguishes between ether and metether ("Uräther"); this latter forms a uniform continuity and represents an absolute, motionless coordination system; whereas the ether itself accompanies matter, every atom is surrounded by a certain, though not constant quantity of the ether, which moves with it. If an atom radiates, this ether accompanies the light wave and represents its elec. and magnetic field; a light ray consists, therefore, of light quanta, similar to Einstein's theory; it moves first with light velocity relative to the radiating atom, but changes gradually to "absolute" light velocity relative to the metether. Together with the fundamental relation between mass and energy $M = E/c^2$ (which L. develops independently of Einstein), this new ether theory enables L. to come to the same conclusion as Einstein regarding the explanation of the expts. which have been generally credited to the advantage of the theory of relativity.

E. FEINER

The distribution of electrons in heavy atoms. A. DAUVILLIER AND L. DEBROGLIE. *Compt. rend.* 173, 137-9 (1921).—One of the authors has listed the absorption frequencies necessary to account for the emission lines of U on the theory of combinations (cf. C. A. 15, 3936). Each orbit contg. one or more stable electrons represents such a frequency; thus the X-ray spectra of heavy elements are richer. A study is now made of the Moseley curves of absorption frequency of elements W to U, extended by the results of Duane and Patterson and by calcn. on combination theory from the emission line values of Coster and the authors. Details of the points of intersection with each other and with the axis are given, these having an important bearing on the numbers of electrons in the various orbits; and schemes of the authors and of Bohr are compared as follows:

K	L	M	N'	N''	O	P	Q
2 ₁	8 ₁	18 ₁	18 ₄	14 ₄	18 ₃	8 ₁	6 ₁

Large figures represent the numbers of electrons in each orbit and subscripts show the number of energy quanta associated with each. Bohr's N series combines N' and N'' of this scheme, and the authors' O series combines N'' and O. The authors believe that X-ray evidence and many physical-chemical properties are in accord with their scheme.

HARRY CLARK

The explanation of Röntgen spectrum and the constitution of the atom. A. SENGAL. *Physik. Z.* 22, 400-2 (1921).—A reply to a criticism which the author had made on a paper by Vegard concerning atomic models. It consists in a restatement and in an attempt to make clear former views expressed by the author and apparently adds nothing which is new to existing theories of the distribution of the electrons in the atom.

A. W. S.

The constitution of nickel. F. W. ASTON. Cavendish Lab., Cambridge. *Nature* 107, 520 (1921).—By the method of positive-ray analysis it was found possible to demonstrate that the spectrum of Ni consists of 2 lines, the stronger at 58 and the weaker at 60. Ni, therefore, consists of at least 2 isotopes. The intensities of the 2 lines are about in the ratio 2:1; this agrees with the accepted at. wt. 58.88.

W. H. KEEN

The periodic table. A modification more in accord with atomic structure. FRANCIS D. MARGARBY. Oxford. *Phil. Mag.* [6] 42, 287-8 (1921).—It is suggested that the best

gases be placed at the right of the periodic table so that it is clear that they are at the end of each group and that the alkali metals begin a new group with a new electronic ring. S. C. LIXON

Genesis of quantum theory. M. PLANCK. *Nature* 106, 508-9 (1920).—Abstract of an address on the occasion of receiving the Nobel prize for physics. This deals mainly with the history of the development of the theory; how, by studying the thermodynamic aspects of radiations and the significance of entropy from the kinetic point of view, P. was led to the notion of energy quanta. Of all the applications of the theory, P. "gives pride of place to Bohr's spectrum theory." The address concludes with some speculations on the attempts to reconcile the quantum theory with the classical electromagnetic theory. P. leaves the impression that they are as yet far off from any solution of the difficulty.

SAUL DUSHMAN

The quantum theory. S. VALENTINER. *Naturwissenschaft Rundschau Schweiz. Chem. Ztg.* 1921, 357-63.—An account, for non-mathematical readers, of the fundamental ideas of the theory as developed from a study of the laws of radiation. The existence of the universal const. \hbar no doubt "signifies an undiscovered law of nature." It plays an important part in all periodic processes such as those involved in the vibrations of electrons and atoms. Recent investigations by Planck, Sommerfeld, Debye, Born and Bohr have led to the conclusion that in consequence of the existence of this constant \hbar , such atoms, electrons, or other oscillators are capable of moving only in definite orbits for which the energy difference is equal to $h\gamma$ (where γ is a frequency). These special orbits are known as "quantum paths." The application of these views by Bohr to account for the spectral series is also discussed. In conclusion V. points out that we do not yet have any physical interpretation of the significance of \hbar . S. D.

Ether and the quantum theory. H. S. ALLEN. *Proc. Roy. Soc. Edinburgh* 41, 34-43 (1921).—According to Sommerfeld's hypothesis the steady motions of any dynamical system satisfy equations of the form $p\dot{q} = nh$, where \hbar is Planck's const., q and p denote the Hamiltonian positional and impulse coördinates, resp., and n is a positive integer. If we regard the const. \hbar as an angular momentum, it is possible, as shown by S. R. McLaren (*Nature* 92, 165 (1913)), to identify this const. with the angular momentum of the magneton. From this it follows that for a magneton of any shape of cross section $N_s N_m = nh$, where N_s denotes the number of tubes of elec. induction, and N_m the number of tubes of magnetic induction. Assuming the charge on unit tube of magnetic induction to be equal to e , this relation becomes $N_m = n(\hbar/e)$. The quantity \hbar/e which defines the unit magnetic tube is equal to 4.120×10^{-1} C. G. S. units. Thus one C. G. S. line of magnetic force (one "maxwell") contains 2.43×10^{-8} unit, or "quantum" tubes. The assumption of discrete magnetic tubes is in accordance with the older views of Faraday and Maxwell, and the view is suggested that this conception may lead to a new mode of representing the luminiferous ether which is in line with Maxwell's suggestion of the rotatory character of magnetism and the gyrostatic models of luminiferous working of the ether which were suggested by Kelvin and Larmor. The relations derived above suggest that "the distinguishing feature of the magnetic tube is a spin about an axis in the direction of its length." Such a view is consistent with Bohr's theory of stationary orbits and Sommerfeld's later development of that theory, according to which the stationary paths of the electrons in the atom form not a continuum, but a net-work. The size of the mesh of this net-work ("phase-space") is determined by Planck's \hbar , and "on the present hypothesis the net-work is formed by the magnetic tubes, between and around which the electrons are able to circulate." S. D.

Determination of quanta conditions by means of adiabatic invariants. G. KRUTKOW. *Proc. Acad. Sci. Amsterdam* 23, 826-37 (1920); cf. *C. A.* 11, 3136.—Mainly mathematical. K. develops the conditions which must obtain in order that the quanta

functions shall have a meaning which is independent of the system of coördinates. This must hold true if the quanta laws are really physical laws. SAUL DUSHMAN

Determinations of atmospheric electricity at Seeham (Salzburg) and at Innsbruck. E. v. SCHWEIDLER. Innsbruck. *Jahrb. Radioakt. Elektronik* 18, 1-21(1921).—A complete summary of previously published work with some more recent similar work. See *C. A.* 14, 148 and *Sitzs. Akad. Wiss. Wien Abt. IIa*, 125, 997(1916); 129, 919(1920).

G. L. WENDT

Radium. R. B. MOORE. *Mineral Ind.* 29, 615-20(1920).—A discussion of production and technical developments. A. BURRS

The significance of radium. R. A. MILLIKAN. *Science* 54, 1-8(1921).—A lecture on the discovery of Ra and radioactivity and the application of the phenomenon of atomic disintegration, discovered by studying the properties of the radioactive elements, to varied fields of scientific investigation. ARTHUR COHEN

The designation of the radium equivalent. N. ERNEST DORSEY. U. S. Bur. Standards. *Nature* 107, 40(1921).—Attention is called to the need for a name to denote that amt. of a radioactive element that produces transformed atoms at the same rate as they are produced by 1 g. of Ra. The curie already denotes this quantity of Ra Em, and the adoption of a new name that would apply to all the radioactive elements would give 2 names for the same quantity of Ra Em. It is suggested that the curie be redefined so as to cover the whole field. W. H. ROSS

Important but unnamed radioactive quantity. N. ERNEST DORSEY. *Science* 54, 193(1921); *J. Washington Acad. Sci.* 11, 381-6(1921).—See preceding abstract.

L. D. ROBERTS

The constancy of the ratio between U X and U Y in uranium of various origins. G. KIRSCH. *Sitzs. Akad. Wiss. Wien Abt. IIa*, 129, 300-34(1921).—U X, and U Y are sepd. with Zr or Ce from uranium minerals of 5 different origins. The half life and transformation const. are for U X: $T = 23.82 \pm 0.075$ days and $\lambda = 3.367 \cdot 10^{-7} \text{ sec.}^{-1}$; for U Y: $T = 24.64 \pm 0.27$ hrs. and $\lambda = 7.814 \cdot 10^{-6} \text{ sec.}^{-1}$. From the ratio U X:U Y, which is const. within 1%, it is found that 4.2% of the U series branches into the Act series. This agrees fairly well with the value of Hahn and Meitner for the ratio of protactinium to Ra (3%), but is incompatible with the old value of 8%. MARIE FARNSWORTH

The radioactivity of some Swiss stones. I. HANS HIRSCHI. *Vierteljahr. Naturforsch. Ges. Zurich* 65, 209-47(1920).—Fourteen stones were examd. for radioactive nuclei and for radiohalos. Extensive tables and photomicrographs are given. *Ibid* 545-72. A general account of radioactivity and methods of measuring it. M. F.

Wasting of radium. G. BERNDT. Berlin. *Chem. Zeit.* 45, 505-6(1921).—A plea for the use of meso-Th and radio-Th in luminous paints in place of Ra, pointing the much greater efficiency of the former, the extinction of the luminescence of the sulfide constituent long before the Ra is exhausted, and the loss of some 8 g. of Ra in paints during 1918 alone. Ra should be conserved for medical purposes where it usually cannot be replaced by meso-Th. G. L. WENDT

The concentration of the radioactivity of ferrous residues from hot springs. F. HENRICH. Erlangen. *Ber.* 54B, 1715-22(1921).—While the active substance of these residues is pptd. with Fe(OH), the soln. can be greatly concd. by evapn. with concd. H_2SO_4 . The sulfates which ppt. or crystallize are inactive. The remaining liquor can then be pptd. with Fe(OH), removing all activity. The process can be repeated on these concd. ferric ppts. The activity is probably largely due to radio-Th. G. L. WENDT

The dimensions of the alpha particle and the deviations from Coulomb's law in the immediate vicinity of electric charges. ADOLF SAMKAL. *Sitzs. Akad. Wiss. Wien Abt. IIa*, 129, 455-81(1920).—The qual. properties of Lenz's model of the alpha particle

(*Münchener Ber.* 1918, 355) are consistent with Rutherford's work on the distribution of H atoms projected at high velocities after collision with alpha particles. But calcd. with Coulomb's laws of force it is some three orders of magnitude too small in energy content. From the law of force e/r^2 , the radius becomes less than 1.6×10^{-13} cm., in agreement with Rutherford's max. of 3 or 1.7×10^{-13} , and the energy content becomes adequate. At a mean distance of 1.8×10^{-13} cm. the force acts as $e/r^{4.117}$. From the space distribution thus detd. approx. at wts. can be calcd. and that for Rutherford's hypothetical H isotope is given as 1.991 as max. If this is the case the disruption of N atoms results only in the usual H nuclei. The inconsistency of the demand of X-ray spectra that the K-series demand 3 inner electrons in the atoms while all other considerations allow only 2 is not resolved by this application of non-Coulombic force laws. The reasons for the deviations from Coulomb's law are discussed. There is reason for supposing that for very short distances the term n in the equation used must be between 2 and 3 in value.

G. L. WENDT

The distribution of emission intervals for alpha particles from polonium. MME. MARIE CURIE. *J. Phys. Radium* 1, 12-24(1920).—A photographic record of 10,000 successive single emissions of alpha particles from a film of Po made by Rutherford's method of electrometer deflections at the critical voltage, the ionization by the particle being greatly magnified by collision ionization. Measurements of the emission intervals show an exact accord with the probability law $N = N_0 e^{-\lambda t/\tau}$, where N_0 is the total number of particles emitted, θ is the mean interval, and N is the number of intervals of greater duration than the time τ . Incidentally these measurements give a new and very exact *redund. of the radioactive constant of Po*, such that λ , the constant, is 0.00496/day, L , the av. life, is 202 days, and P , the half-life, is 140 days. G. L. WENDT

A reciprocating expansion apparatus for detecting ionizing rays. T. SHIMIZU. *Proc. Roy. Soc. London* 99A, 425-31(1921).—A modified form of the Wilson app. for making visible the tracks of ionizing rays was used. Other liquids than water, such as ale. and petroleum, were tried, with similar results. In obtaining the most accurate shape of the tracks the Wilson original app. is superior, but for detecting the rays the new app. has great sensibility. An α ray can be neglected during an X-ray measurement. L. D. ROBERTS

Branched α -ray tracks. TAKEO SHIMIZU. *Proc. Roy. Soc. London* 99A, 432-5 (1921).—The reciprocating expansion app. described in the preceding abstract was used. The eye could detect branched tracks different from spurred tracks photographed by C. T. R. Wilson. A cinematographic film was used. The camera was operated by the shaft connected to the expansion chamber. The mirror system of the camera projected simultaneously two images of the object. A sketch is given. Two photographs, mutually perpendicular views of the same track of a polonium α -ray, are shown. 3,000 α -ray tracks were photographed. Eleven were branched and 35 were spurred. The branched tracks were very much alike, a single branch being at the end of the path. The abrupt bending takes place at different places in the spurred tracks. The work was done with E. Rutherford.

L. D. ROBERTS

Stoppage of α -rays of elements and compounds. H. RAUSCH V. TRAUBENBERG. *Z. physik* 5, 396-408(1921).—W. H. Bragg's conclusion that the stopping power of an element is proportional to the sq. root of its atomic number is tested by the available data, including that of T. and Philipp (cf. following abstract). There is found to be a systematic deviation which increases with the atomic number. The additive law for compds. is not exact.

F. C. HOYT

Two direct methods for the determination of the range of α -rays in liquids and gases. H. RAUSCH V. TRAUBENBERG AND K. PHILIPP. *Z. physik* 5, 404-9(1921).— α -Rays from a source below the surface of a liquid strike a screen of sidot above the surface,

and produce scintillation. The level of the liquid is raised to extinction of this effect, and the range can be calcd. with the aid of a slight correction for the air layer. For distd. water the value found is 60.0μ . For gases the method consists in letting the rays produce scintillation on an inclined plate, the distance being calcd. from the position of the line where scintillation stops.

F. C. HOTT

The study of ionization in gases. H. GREENACHER. *Physik. Z.* 22, 289-94, 294-7 (1921).—Description and discussion of expts. suitable for demonstrating various ionization phenomena in gases, such as those due to collision, thermionic effects, photoelec. effects, flames, etc., and phenomena observed with a. c., such as electrodeless ring discharge, etc.

ARTHUR COHEN

The ionization of gases during chemical reaction. II. A. PINKUS AND M. DE SCHWARTZS. *Helvetica Chim. Acta* 4, 288-95 (1921); *J. chim. phys.* 18, 366-411; cf. *C. A.* 13, 207.—The following reactions have now been studied: $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$; $2\text{O}_2 \rightarrow 3\text{O}_2$; $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2$; $\text{NO}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}_4$. In all cases ionization was proved. Two conclusions are reached: (1) Chem. action can give an intense bipolar ionization in the gas in which the action takes place, which is independent of any ionization produced by physical means. (2) The ionization produced is proportional to the speed of the chem. reaction.

ROBERT S. LANDAUER

The ionization of gases during chemical reaction. III. A. PINKUS. *J. chim. phys.* 18, 412-3 (1920).—A criticism of the work of Trautz and Henglein (*C. A.* 14, 3362), who had failed to observe elec. cond. imparted to a gas mixt. by its reaction in the cold. P. suggests that the ionization of the mixt. is greatest at the moment of mixing and first reaction but dies out rapidly thereafter. Cf. preceding abstract. G. L. WENDT

Theory of the vacuum discharge. G. JAFFE. *Ann. Physik* 64, 733-44 (1921).—A further development of the theory previously given (*C. A.* 15, 1251) in the direction of higher pressures, through consideration of the lengths of the paths of the electrons. The current-voltage relations derived are similar to those given in the first paper, but the manner in which these vary with the pressure is different. The voltage required for any definite current increases with pressure. For large current-densities the three-halves law is approached as a limit. Assuming that the thermal velocities of the electrons are not negligible compared with those acquired because of the elec. field, J. finds that when the current density is large it varies as the square of the voltage, that is, at higher pressures the current increases more rapidly than in accordance with the three-halves power law. From these considerations it is possible to account for Lilienfeld's observations (*C. A.* 7, 3488).

SAUL DUSHMAN

Remarks on Jaffe's paper on "The theory of the vacuum discharge." J. E. LILLENFELD. *Ann. Physik* 64, 745-9 (1921).—A criticism of Jaffe's paper (preceding abstract) in which L. points out that no account has been taken by the former of the observations made by him on the behavior of insulators in an elec. discharge tube (*C. A.* 14, 3017).

SAUL DUSHMAN

The disappearance of gas in the electric discharge. III. N. R. CAMPAGNA, et al. *Phil. Mag.* [6] 42, 227-46 (1921); cf. *C. A.* 15, 468, 2779.—Most of the present paper is devoted to the disappearance of CO according to the formula $2\text{CO} = \text{CO}_2 + \text{C}$. In attempting to establish a relation between ionization and quantity of chem. action, it is found that neutralization of the positive ion at the wall of the discharge vessel plays a large part, which must be taken into account. This was done by silvering the inner wall and collecting current from the grid thus formed. A marked increase in the grid current just as the "glow" potential is reached shows that there is a relation between chem. action and ionization which did not appear evident when the grid current was neglected. From a study of the rate of "clean up" under different conditions, the conclusion is drawn that the reaction consists in the combination of one positive ion

of CO with a neutral mol. This would demand the disappearance of two mols. of CO for each positive ion formed. The exptl. verification of this prediction is beset with many difficulties, such as reversal of the reaction by reduction of the CO₂ formed, by the hot W cathode or by the C resulting from the reaction. The possibility of both of these reactions was demonstrated, though the efficient collecting of CO₂ by the liquid-air trap indicates they are not the principal disturbing causes, but the reversal of the reaction by the action of the discharge on the CO₂ condensed on the walls acting as an anode. A new tube arranged for the rapid removal of CO₂ by liquid air gave at all pressures from 0.3 down to 0.03 mm., a value very close to 2.0 for the ratio of CO mols. disappearing to the number of ions formed. On account of the possibility of chem. action in the gas phase and on the walls, it is believed that the general applicability of Faraday's Law in its usual form to gaseous reactions under elec. discharge is illusory. The question as to the origin of spectral lines is also raised, as it does not appear from the present results that they can be due to the complete removal of an electron and its recombination.

S. C. LIND

Ionization potential and the size of the atom. A. S. EYR. McGill Univ. *Nature* 107, 552-3(1921).—A comparison of the results that have been compiled on the ionization potential, the diam. of the atom as calcd. by Bragg (*C. A.* 14, 3584) and the cube root of the at. vol. shows that for the first group of the elements the products of the ionization potential with the diam. and with the cube root of the at. vol. are fairly concordant. It may, therefore, be concluded that the work done in the removal of an exterior electron is nearly proportional inversely to the radius. The same remark also applies to the elements Mg, Ca, Sr and Ba of Group II, but considerable divergence is shown in the values for the other members of this group. The values of certain elements in Groups III to VII are given for comparison but the knowledge of ionization potentials is as yet too fragmentary to permit of definite conclusions. W. H. ROSS

The excitation of light and the ionization of atoms and molecules through the impacts of slowly moving electrons. J. FRANCK. *Physik. Z.* 22, 388-91, 409-14, 441-8, 466-71(1921).—The paper gives an excellent summary of the most recent developments in the field of ionization and resonance potentials. The subject is treated from the point of view of F.'s own exhaustive expts. and contains much recent material not easily accessible. In summing up the paper he concludes that the recent researches have contributed markedly to the following fields. (1) The great numbers of detns. (especially those of his pupils and himself) of excitation and resonance potentials in monatomic gases have been in such close agreement with Bohr's interpretation of the laws for series spectra that taken as a whole they compose an excellent method for the detn. of "k." (2) They lead to an extension of, and an excellent check on, the optical method of detg. series relationships. They lead in some cases to the discovery of new series lines in regions which cannot be investigated by optical means. (3) They furnish a means of a direct test of the correctness of atom models. (4) They lead to the establishment of the existence of excited atoms in a metastable state. (This metastable state may be of considerable interest to those interested in the mechanism of chem. gas reactions.) (5) They lead to a proof of the existence of close relationships between the ionization and dissociation of polyatomic gases. L. B. LOHN

The effects of impurities on the ionization potentials measured in thermionic values. L. S. PALMER. *Radio Rev.* 2, 113-25(1921).—The method of investigation used is based on a study of the current-voltage curves measured in hard and soft 3-electrode tubes. The details of the method have been given in a previous paper. Certain bends in these curves are interpreted as being due to the bombardment of the filament by positive ions. P. is thus enabled to det. the ionization potentials of the gases He, H₂, and A used in filling the tubes. There are variations in the values for the ionization potentials

obtained in He. These are ascribed to impurities, and the amt. of impurity active accords with the values found by Horton in He. This effect of the impurity also explains the low values of the potentials obtained in Stead and Goslings work. The characteristic of the soft 3-electrode tube can be used to det. the resonance and ionizing potentials of the contained gas. The nature of the gas and presence of the impurities can be detd. from the critical points of the characteristics. Methods of measuring ionization potentials are liable to error if impurities are present. Horton's previous work is confirmed and the result has been extended to A with traces of Hg. The value of the ionization potential decreases slightly with increase of gas pressure, causing changes in the characteristics similar to those for impurities. A number of the critical potentials obtained for He and A are given.

L. B. LOGG

Minimum discharge potential in hydrogen at low pressure. EMMANUEL DUBOIS. *Compt. rend.* 173, 224-5(1921).—Using a hollow cylinder and an axial wire as electrodes D. attempted to measure the minimum potential difference required to produce discharge in very pure H at low pressure. Occlusion of gas in the wire accompanied discharge and caused the critical voltage to rise. A series of detns. in which the wire was used alternately as anode and cathode showed a rapid increase of voltage for one set (wire as cathode) and a slower increase for the other set (wire as anode). Wire could be cleaned up by heating to dull redness. Various metals were used with similar results.

HARRY CLARK

Minimum discharge potential in hydrogen at low pressures. EMMANUEL DUBOIS. *Compt. rend.* 173, 233-4(1921).—The emission of occluded gas by the electrode under the influence of heat is not so simple as was believed (cf. preceding abstract). Although a dull red heat cleans up the wire well, a white heat does not; the results of minimum discharge voltage measurement are nearly as inconsistent in the latter case as when no attempt is made to clean it. After a white heat the wire may be cleaned by a red heat or by a few hours' rest. The view is discussed that the gas may exist in and on the metal in soln. and in chem. combination.

HARRY CLARK

The influence of slight impurities on the sparking potential in air. EDGAR MEYER. Zurich. *Ann. Physik* 65, 335-68(1921).—The chief variations in potential are caused by variations in water vapor.

G. L. WENDT

The influence of water vapor in sparking potential. HILDEGARD STÜCKLEN. Zurich. *Ann. Physik* 65, 369-77(1921); cf. preceding abstract.—Minimal traces of water vapor such as are furnished by the persistent water adsorbed on glass surfaces suffice to alter the sparking potential markedly.

G. L. WENDT

"The effect of a uniform magnetic field on the motions of electrons between coaxial cylinders." ALBERT W. HULT. *Phys. Rev.* 18, 31-57(1921).—The equation of motion for electrons starting from a cylindrical cathode towards a coaxial cylindrical anode in a uniform magnetic field parallel to the common axis is deduced. The electrons reach the anode if the ratio of the p. d. to the magnetic field is greater than a critical value, and fail to reach it if the ratio is less than this value. In the case of a small cathode in the axis of an anode of radius R , at a potential V the critical magnetic field is $H = \sqrt{(8m/e)} (V^{1/2}/R)$. For a small anode of radius r_0 , at a potential V , in the axis of a cylindrical cathode of radius R_0 , the critical field is $H = (r_0/R_0) \sqrt{(8m/e)} (V^{1/2}/R_0) + (2mv_0/eR_0)$. The equation applies with appropriate R_0 , and e/m , to the positive ions produced by electrons from an internal cathode. If both cylinders are of large radius the formula reduces to the familiar one of plane parallel plates. The equation of the path is deduced on the assumption that the space charge is the same as that without the magnetic field. The path is given by the equation $r = R(\sin \beta_0)^{1/2}$. This is a close approximation to the path as calculated from the space charge distribution recently worked out by Langmuir. Experimental curves showing the current at a constant

pressure as a function of the magnetic field for different anode diameters, voltages, filament temps., and degrees of symmetry are in agreement with the theory within the limits of experimental error.

L. B. LOSS

Theory of the motions of electrons between coaxial cylinders taking into account the variation of mass with velocity. LEIGH PAGE. *Phys. Rev.* 18, 58–61(1921); cf. preceding abstract.—If the fields are high it becomes necessary to take into account the variation of the mass of the electrons with velocity. Putting the expression for longitudinal and transverse mass into the equation of motion and integrating it, $e_0/m_0 = 8\pi^2 c^4 R^4 V / (N^2 - 4\pi^2 R^2 V^2)$. This depends on the larger radius R , on the total magnetic flux N , and on the total potential drop V , and is not affected by the space charge. Because the longitudinal mass is involved the equation provides a method of experimentally verifying the theoretical expression for longitudinal mass.

L. B. LOSS

The effective cross-section area of gas molecules toward slow electrons. CARL RAMSAUER. Heidelberg. *Ann. Physik* 64, 513–40(1921).—A comparison of the relative magnitudes of the complete absorption of slow-moving electrons by gas mols., i. e., their complete removal from the stream, with the deflection, diffusion or velocity reduction also caused by the same mols. The absorption measurements are those of Mayer (*Ann. Phys.* 64, 451(1921)). The two effects are found to be identical in magnitude so that the total effective cross section of the mols. is identical with their absorbing cross section. These are for air, H₂, N₂, H₁, and A, resp., 890, 1260, 920, 550 and about 100×10^{-18} cm². The figures for A are not consistent but confirm the abnormally small area of this mol. The fact that the effective vol. of the mol. is no greater than the absorbing vol. shows a definite surface beyond which electrostatic forces become ineffective, especially since this effect is most marked in the case of H₂, in which the force fields are presumably least closed. The small values for A indicate a high penetrability of this atom for slow electrons. The electron velocities used were in all cases approx. 1 v.

G. L. WENDT

Mobilities of ions in helium at high pressure. J. C. MCLENNAN AND E. EVANS. Toronto. *Trans. Roy. Soc. Canada* 14, Sect. III, 19–26(1920).—Pure He at high pressure does not exhibit any appreciable metallic elec. cond. Mobilities of positive and negative ions produced in He at a pressure of 81 atm. by α -rays from Po are, resp., 2.52×10^{-2} and 4.28×10^{-2} cm. per sec. per volt per cm. They do not vary inversely with the pressure at high pressures.

A. T. CAMERON

Negative canal rays and the alteration of charge in gas mixtures. J. KOENIGSBERGER AND A. RÜTTENAUER. *Physik. Z.* 22, 193–200(1921).—The transformations of H[−], H⁺ and H atoms in H₂ and Hg vapor are studied and shown to be comparable with the equations developed. Neutral atoms have a greater radius than corresponds to a single-quantum velocity. The negative H ion loses an electron more easily than the neutral Hg atom but the latter has a strong effect on the positive H ions. Negative H₂ ions were not observed and their existence is doubtful.

G. L. WENDT

Thermal and electric conductivity of metals. WALTER MEISSNER. *Jahrb. Radioakt. Elektronik* 17, 229–73(1921).—A review of recent investigations. The following topics are included: Measurements of the thermal and elec. cond. of the same metal; the relations between elec. cond. and temp., pressure, and magnetism; the relations between the elec. resistance and the sp. heat from the point of view of the periodic system. A theoretical part considers the modern theoretical contributions, especially the works of Haber, Planck, Grüneisen and Borelius. A complete literature index is attached.

E. FRÄZER

Electric conductivity of metals and alloys. W. GUGATZKE. *Jahrb. Radioakt. Elektronik* 17, 276–92(1921).—A reply to C. Benedicks (*Jahrb. Radioakt. Elektronik* 13, 351(1917)). G. emphasizes his former statements, that theoretically the elec. cond. cannot

be expected to be a linear function of the compn. of the alloy, and that the deviations are greater, the greater the difference between the elec. cond. of the components of the alloy. If the crystals of the alloy are arranged parallel to the direction of the elec. current, the elec. cond. will approach a linear function, whereas if the elec. current passes through in vertical direction the elec. resistance will approach a linear function of the compn. of the alloy.

E. FISCHER

The electric conductivity in metallic aggregates. CARL BENEDICKS. *Jahrb. Radiakt. Elektronik* 17, 292-8(1921).—Reply to W. Guertler (see preceding abstract).

The electric conductivity in metallic aggregates. W. GUERTLER. *Jahrb. Radiakt. Elektronik* 17, 298-9(1921).—Reply to C. Benedicks (see preceding abstract). E. F.

Use of three-electrode lamp (Triode) for measuring ionization currents. J. MALLASZEW. *Compt. rend.* 172, 1093-4(1921).—M. describes connections for amplifying the ionization current produced in a gas by X-rays, by having the ionization currents charge up positively the grid which is normally maintained at a negative potential. In using the arrangement it is essential that the normal leakage current from the grid be very small compared with the ionization current to be measured. S. DUSHMAN

New forms of technical electron tubes. C. R. FORTH. *Jahrb. Radiakt. Elektronik* 17, 174-8(1920).—A description of some new models of the C. Lorenz Co. Berlin-Tempelhof.

E. FISCHER

The action of the silicon-carbide detector. F. LUCHSINGER. Zurich. *Physik. Z.* 22, 487-91(1921).—The electrolytic explanation of the action of this detector advanced by Huizinga (*Physik. Z.* 21, 91(1920)) is inadequate because no electrolytic decompn. can be detected at the contact point and because the action of the detector is unaffected by temp. changes ranging from 870° to the temp. of liquid air.

G. L. WARD

Magnetism and the structure of atoms. O. v. AUWERS. *Jahrb. Radiakt. Elektronik* 17, 181-229(1921).—A review with a complete literature index. The electron theory of diamagnetism and paramagnetism of Langevin and the magneton-theory of P. Weiss are thoroughly discussed and the theories of W. Voigt and R. Gans briefly considered. The relations between chem. constitution and the magnetic properties as studied by Tammann, Pascal, Wedekind, Rosenblum and others are summarized and the importance of the magnetic analysis of A. Quararoli is emphasized. The results of Hensler on the influence of physical conditions on the magnetism of alloys are fully reported.

E. FISCHER

Electron theory of magnetism. S. J. BARNETT. *Science* 53, 465-75(1921).—An excellent summary of the different theories, including those of Langevin, Gaus, Keesom, and others. The expts. of the author and of Einstein and de Haas are described, and the probable explanation of cosmical magnetism is discussed briefly. SAUZ, DUSHMAN

A theory of physical phenomena at high temperatures, with applications to astrophysics. MECH N. SAHA. *Z. Physik* 6, 40-55(1921).—S. makes some deductions from the consideration that at high temps. the atoms of a gas are ionized by thermal impacts alone. A relation between ionization voltage and degree of ionization at a given temp. can be found by thermodynamics. The absence of pure temp. radiation in the permanent gases can be accounted for by their high ionization voltages. The dependence on ionization voltage also explains why the spectrum of a star depends on its superficial temp.

F. C. HOTT

Effect of an electric current on the photoelectric effect. FRANK HORTON. Univ. London. *Phil. Mag.* [6] 42, 279-80(1921).—A note expressing the view that the supposed effect of an elec. current on the photoelec. effect of a Bi plate as described by Shenstone (*C. A.* 15, 2782) was probably due to the liberation of gas from the plate by the heating effect of the current. The applied p. d. of 14 v. would be sufficient to cause radiation (and possibly ionization) of the liberated gas. This radiation would act on

the plate to enhance the liberation of electrons, which would produce further radiation and so a considerable increase of photoelec. current might be produced even with a Hg-vapor pump in operation. On stopping the current through the plate, gas liberation would cease, and pumping would quickly lower the gas pressure and hence lower the photoelec. effect.

S. C. LIND

The distribution of energy in continuous Röntgen-ray spectra. A. MARCH. *Physik Z.* 22, 429-38(1921); *Ann. Physik* 65, 449-60(1921).—The distribution of energy in the Röntgen-ray spectrum is of interest because the physical and biol. effects depend on the way in which the energy is distributed among the wave lengths as well as on the intensity of the radiations. Since absorption changes with the wave length the fraction of the energy penetrating to a given distance beneath the surface of a body depends on the distribution of the energy in the spectrum. The case in which the radiations are excited at const. voltage is first considered. The expression previously developed for this case is verified by means of observations by Ulrey after correction has been made for absorption by the glass wall of the tube. This expression also gives the energy for variable voltages lying in the neighborhood of the max. voltage as in the Liliendt tube or in self-hardening tubes. The distribution of energy in the Coolidge tube demands special consideration. The same expression gives approx. the distribution of energy when the radiation is excited by an alternating voltage. Hence the distribution of the energy in the spectrum is nearly independent of the voltage curve and is detd. by the max. value of the voltage. Whatever the periodicity of the voltage the character of the radiation is nearly the same as that excited at a const. voltage equal to the max. voltage. The distribution of energy in a continuous Röntgen-ray spectrum is uniquely defined by the shortest wave length λ_0 , a result which is important in methods of radiography and radiotherapy. The action of metal filters rests on the fact that by them the long wave lengths are weakened more than the short ones. The intensity of a wave length λ is changed through filtering from K_λ to $K_\lambda e^{-\alpha d}$ where α is the coeff. of absorption and d the thickness of the filter. The coeff. of absorption depends on the wave length in such a way that $\alpha = k\lambda^{2.4}$. For wave lengths below the absorption band of the K-series k is detd. by the density and at. wt. of the element. Two filters are equiv. to each other if $k_1 = k_2 d_2$. With increasing strength of the filter the position of the max. of the intensity of radiation is shifted toward the shorter wave lengths. Hence the filter acts on the spectral distribution as an increase in voltage acts on this distribution. The displacement of the max. by the filter is proportional to the strength of the filter and is greater for long than for short wave lengths. A. W. S.

Structure of the L series. A. DAUVILLIER. *Compt. rend.* 172, 915-7(1921).—Using a quartz X-ray tube of the Coolidge type with mica window, the tube operated at const. voltage ($\pm 1\%$), and spectrometer of great dispersion, D. studied the L series of uranium. Only 8 lines were previously known. Nine new ones were found, of which 7 are known in lighter elements. Nomenclature of lines is discussed. Six Sommerfeld doublets were identified. Moseley curves, now extended to U, show necessary changes in classification of L lines of tungsten. Emission and absorption spectra of U were photographed on the same plate. L_1 between β_1 and β_2 , and L_2 and L_3 , resp., were slightly shorter than the series heads γ_1 and γ_2 . The L_1 series, isolated by proper const. voltage, contains β_1 , β_1' , β_1'' , ν_1 , α_1 , α_2 , and L. L_1 lines are strong and fall on straight Moseley plots; L_2 lines are weak and fall on curved plots; L_3 lines are strong and fall on curved plots. HARRY CLARK

The L series of uranium and the principle of combinations in X-ray spectra. A. DAUVILLIER. *Compt. rend.* 172, 1350-3(1921).—The line β_2 of the L_1 series of U is found to have 2 satellites, β_2' and β_2'' . This makes a total of 9 lines at present known to belong to L_1 . Working at const. voltage (21450 \pm 50), D. sepd. the L_2 and L_3 series.

He found 6 lines in L_2 and 9 in L_4 . Nomenclature of the L series lines is rediscussed. To account for the known lines of W and U on the principle of combinations (that the frequency of each line is the difference between 2 critical absorption frequencies) it is necessary to assume the existence of no less than 16 critical frequencies as follows—K, L_2 , L_3 , L_4 , M_2 , M_3 , M_4 , M_5 , M_6 , N_7 , N_8 , N_9 , N_{10} , N_{11} , and N_{12} . A careful detn. of the L_1 absorption frequency and the frequency of the line β_2 gives the value of N_4 corresponding to 200 Å. A photograph of the absorption spectrum of U in the neighborhood of L_1 made with great dispersion shows a sharp, distinct, white absorption line just at the edge of the L_4 discontinuity. The width of this line is the same as that of the emission lines obtained with the same app.

HARRY CLARK

The principle of combinations, and absorption lines in X-ray spectra. A. DAUVILLIER. *Compt. rend.* 173, 35-8(1921).—Some redetns. are described of L series lines, presumably of U, though this is not explicitly stated. The principle of combinations is discussed again and the system of 16 critical frequencies previously described (cf. preceding abstract) is altered to include 2 new frequencies, O_x and O_y. The last part of the paper deals with absorption lines. The white line at the L_1 absorption discontinuity of U has been described. Another phenomenon of similar origin is now presented—the K absorption frequency of Br lies between the frequencies of the $L_{\alpha\alpha}$ and $L_{\alpha\gamma}$ of U. When these 2 lines are photographed a 3rd black line occurs between them at the discontinuity of the Br in the photographic plate. This line changes from black to white when a filter of KBr is used.

HARRY CLARK

Soft characteristic X-rays from arcs in gases and vapors. F. L. MOHLER AND PAUL D. FOOTE. *J. Wash. Acad. Sci.* 11, 273-4(1921).—The authors have studied the stages in the discharge between a hot cathode and anode in a vapor at low pressure by measuring the photoelec. effect of the radiation on 2 other electrodes entirely shielded from the ions produced in the arc. This photoelectric current plotted as a function of the exciting voltage shows nearly a linear relation with changes of slope at critical potentials. In this manner potentials have been found which are detd. by the limiting frequency of the softest X-ray series of a number of elements. The observed potentials and the corresponding wave lengths for these X-rays are given for Na, Mg, P, S, Cl, C, N and K. Two critical potentials were found for each of these elements except C and N. A plot of $\sqrt{1/\lambda}$ (where λ is the wave length) against the atomic number for Mg, P, S, and Cl shows that there is a proportionality between $\sqrt{1/\lambda}$ and the atomic number within the probable observational error. The points for the second series for these elements lie on a nearly parallel line. They indicate a new X-ray series of feeble intensity. The limits L_α of the L series for light elements were computed from X-ray spectral data by the relation $L_\alpha = K_\alpha K_\alpha$. The value L_α for Na falls above the extrapolated straight line but is in agreement with Millikan's recent observation of the L_α as $\lambda = 372$ and 378 Å. The K limits found for C and N agree with the extrapolated K_α line and the value of 45.4 Å. for C agrees with the value 42.6 Å. found by Kurth. This method is of value in studying radiations between the range of the vacuum spectroscope and the X-ray crystal spectrometer.

A. W. SMITH

The laws of absorption of X-rays. F. K. RICHTMYER. *Phys. Rev.* 18, 13-30(1921).—This is a very careful exptl. study of the absorption of X-rays by H₂O (oxygen), Al, Cu, Mo, Ag and Pb, each over a great part of the range of wave lengths 0.093 Å. to 0.95 Å. The longest of these waves is shorter than the critical K absorption wave length of O, Al, or Cu, and falls between K and L for Mo, Ag, and Pb. Rays from a Coolidge tube were analyzed by spectrometer with NaCl crystal, and the intensity was measured by ionization of MeBr. Scattered and fluorescent radiation from the absorbing screen were suppressed by placing the screen in front of the spectrometer slit nearest the tube. Detailed tables and curves of the results are given. The mass-absorption

coeffs., μ/ρ , of these substances is given by $\mu/\rho = F\lambda^2 + (\sigma/\rho)$ where λ is wave length and σ/ρ is the mass-scattering coeff., except in the region close to λ_K on the short-wavelength side, where the equation gives values which are somewhat too large, the error being greater as the difference between λ and λ_K is smaller. For each substance F has a const. value for $\lambda < \lambda_K$ and another much smaller const. value for $\lambda > \lambda_K$. The mass-scattering coeff. is independent of wave length, and is, to a first approximation, the same for all elements. The atomic-absorption coeff. is given by $\mu_a = 2.29 \times 10^{-37} N^4 \lambda^2 + \sigma_a$, where N is at. number and σ_a the at.-scattering coeff. for $\lambda < \lambda_K$. No trace of the suggested "J" absorption discontinuity was found. At 0.093 Å. μ/ρ for water is still much greater than for the hard rays of Ra C.

HARRY CLARK

Diffraction of X-rays by liquids. A. DUBIERNE. *Compt. rend.* 173, 140-2(1921).—Expts. are described in which a fine parallel beam of X-rays is sent through a layer of liquid sufficiently thick to obscure any diffraction caused by a possible stratification of the mols. near the surface. The direct transmitted beam was absorbed by a bit of lead while the rays scattered or diffracted by the liquid fell upon a photographic plate placed at some distance from the liquid in a plane normal to the original beam. Hg, MeI, CH₃I, C₂H₆, C₂H₅Br, and various mixts. were used; one or more diffraction rings were observed with each. Although the rings suggest the existence of a cryst. structure, many small crystals being oriented at random, it is shown that such an assumption is unnecessary. If it be assumed that the diffracting centers are sep'd. from each other by a fixed distance, as though they were at the centers of little balls the surfaces of which are in contact, the lines of centers being oriented at random, there will be a certain angle of max. intensity of the diffracted light corresponding to each wave length. It is assumed that the diffracting centers are mols. the distances between the centers of which are const. except for small thermal movements.

HARRY CLARK

Crystal structure of the silver halides. R. B. WILSEY. Eastman Kodak Co., Rochester, N. Y. *Phil. Mag.* 42, 202-4(1921).—The crystal structure of the Ag halides has been detd. by the powder method of Debye (*C. A.* 11, 1786) and Hull (*C. A.* 12, 649). AgBr gave the pattern of a simple cube, one atom being associated with each point of the cubic lattice. AgI has the same diffraction pattern as diamond; each I atom is at the center of a tetrahedron the corners of which are occupied by 4 Ag atoms, and each Ag is surrounded by 4 I atoms in the same way.

Substance.	Arrangement.	Side of cube.	Distance of nearest at. centers.	Computed from Bragg's at. diameters.
AgCl	Simple cubic	2.78 Å.	2.78	2.82
AgBr	Simple cubic	2.89 Å.	2.89	2.96
AgI	Tetrahedral	6.53 Å.	2.83	3.17

The Ag salts were pptd. from AgNO₃ by the corresponding K halides, giving flocculent ppts. in which crystals cannot be recognized under the microscope. X-ray analysis, therefore, gives the first proof of the cryst. nature of the ppts. AgCl and AgBr as pptd. in photographic emulsions form crystals which can be recognized as belonging to the cubic system; AgI gives evidence of forming hexagonal crystals.

S. C. LIND

Formation of mixed crystals by the contact of solid phases. L. VEGARD. *Z. physik* 5, 393-5(1921); cf. *C. A.* 15, 2787.—Mixts. of two powdered crystals that have not been ground together show a superposition of the spectra of the components when exmd. by the Hull-Debye method of X-ray analysis. On grinding together, however, they show the single spectrum characteristic of mixed crystals. The lines are not sharp, as the mixed crystals thus formed by contact are not homogeneous in constitution.

F. C. HOYT

Luminescence at high temperatures. E. L. NICHOLS AND D. T. WILSON. *Proc. Nat. Acad. Sci.* 6, 693-5(1920).—Luminescence has been discovered at temps. above

those at which ordinary phosphorescence disappears and fluorescence excited by light reaches extinction. The glow is excited by contact with the outer zone of the H flame, although it may also be produced by cathode bombardment and the action of X-rays. It differs distinctly from photoluminescence in many respects. It is observed in many substances such as CaO, MgO, Al₂O₃, etc., with which photoluminescence is not observed. It is absent in some strongly fluorescent materials, such as willemite and Ca tungstate. No addition of activating substance is necessary. The effect often occurs at temps. below red heat. When superimposed upon the red heat it is readily distinguishable by the color, which is usually green, blue or white, by the law of decay which is the same as holds for phosphorescence, and by the spectrum, which is a characteristic broad-banded fluorescence spectrum often lacking altogether in the red. The upper limiting temp. differs with various substances, from 52° for Al₂O₃ to 940° for ZnO and pure ZnS. The color of the glow changes with the temp., so that the spectrum changes to shorter wave lengths as the temp. increases. Similar phenomena have been observed for the excitation by cathode rays and X-rays. Fuller details will follow in subsequent papers.

SARL DURSHMAN

A study of the glow of phosphorus. Periodic luminosity and action of inhibiting substances. LORD RAVLEIGH. *Proc. Roy. Soc. London* 99A, 372-84 (1921).—A study has been made of the periodic luminosity propagated through the gas space when the last traces of O are being removed from air by P, or when air is allowed to leak slowly into a vessel contg. P. This intermittent effect requires the presence of H₂O vapor, the glow becoming steady with moderate drying. Water vapor thus inhibits the combination of P vapor and O within certain limits. The action of other inhibitors, such as camphor, NH₃, turpentine and pear oil, has been studied. It is shown that the propagation of the waves of combustion cannot be due to a rise in temp. of one layer igniting the next. It is assumed that the propagation depends upon the provision of nuclei, as in the propagation of crystn. through a supercooled liquid. The inhibitors are supposed to act by taking prior possession of the nuclei, thus rendering them unavailable for propagation. This theory is discussed in detail. H. JERMAIN CREGGTON.

The luminescence of certain oxides sublimed in the electric arc. E. L. NICHOLS AND D. T. WILBER. Cornell Univ. *Phys. Rev.* 17, 707-17 (1921).—Thin films of metallic oxides were obtained by subliming the metal or one of its salts from the crater of a direct-current carbon arc on to a metal disk. Oxides prep'd. by sublimation are found to respond to excitation by cathode rays. The shift in color in luminescence in general is to the violet with increasing temp. The effect of pressure on luminescence is discussed. The most active oxides were those of Ca, Mg, Zn (Zn), Zr, Si and Al. R. S. L.

Magnetic double-refraction of suspensions of powdered crystal in liquids. SR. PROCOPIU. *Compt. rend.* 173, 353-5 (1921).—Expts. with several uniaxial crystals suspended in liquids of the same av. index (list given) have verified the following rule: the double-refraction in a magnetic or elec. field of a suspension of powdered crystal in liquid of the same index is positive if the optical and magnetic (or elec.) signs are alike, and negative if these signs are different. This rule depends on the convention that the optical axis of the suspension is considered to coincide with the direction of the field. If the crystal is magnetically or electrically positive its axis will coincide with the field and the optical signs of the crystal and the suspension will be alike; if electrically or magnetically negative the axis will lie normal to the field and the optical signs of the crystal and the suspension will be opposite. The electric double-refraction was discussed by St. Procopiu, *Compt. rend.* 172, 1172. HARRY CLARK.

The influence of light on the conductivity of fluorescent liquids. H. SOULAN. *Compt. rend.* 172, 581-2 (1921).—Previous attempts to show that light has an influence on the cond. of fluorescent liquids have been negative or inconclusive. If fluorescence

is due to a chem. transformation of the mols., however, continued exposure to light should give a progressive variation in the cond. Soudan finds such an effect in the case of esculin, eosin, and curcumin and quinine. The results are given by an empirical equation $\log(C_{\infty} - C_t) = b - at$ where a and b are consts. independent of the solvent, C is the cond. and t the time. For concd. solns., it does not hold, partly because the converted mols. form a protecting screen around the others in agreement with the theory of Perrin.

FARRINGTON DANIELS

Spectro-radiometric studies of polarization phenomena. I. R. INGERSOLL. *J. Optical Soc. America* 5, 150-9(1921).—An app. for measuring the magnetic rotation of light is described. It is sensitive to 0.001° and accurate to 1% for rotation of a few minutes. Two images of a polarized beam are measured with a bolometer, after passage through a magnetic field. Light from 5μ to 2.3μ may be used. Natural rotation in the case of sugar, etc., is proportional to magnetic rotation (Weidemann's law). The refractive index and absorption index of certain metals are given. Polarization from diffraction gratings is described. A bibliography is included. FARRINGTON DANIELS

A relation between the degree of polarization and the intensity of the light diffused by anisotropic molecules. A new determination of Avogadro's constant. JEAN CABANNES. *J. phys. radium* 1, 129-42(1920).—C.'s earlier expts. with transparent gases proved the approx. correctness of Rayleigh's formula, $J/E = (\pi^2/2\lambda^4) [(\mu^2 - 1)/n]^2 n V$, where E is the intensity of a beam of unpolarized light, J is the intensity of light diffused at right angles, λ the wave length, μ the refractive index and n the number of molecules in the volume V . He derives, here, a more general equation, based on classical dynamics and the electromagnetic theory of light, which allows for the fact that light reflected from anisotropic mols. is polarized. $R = 3\pi^2 [(\mu^2 - 1)^2 / \lambda^4 n] [(1 + \rho)/(8 - 7\rho)]$, in which $R = J/EV$, and ρ = the ratio of intensities perpendicular and parallel to the original ray. Strutt's expts. permit a verification of the calcs. of ρ . The expts. of Fowle on the transparency of the atm. permit a calcn. of R . The value of R is obtained also from unpublished measurements of Cabannes on the intensity of light diffused in argon. Argon being monatomic is isotropic and light reflected from its mols. is not polarized. Substitution in the equation gives $(6.90 \pm .20) \times 10^{21}$ for Avogadro's number, N . Since the value based on the transparency of the atmosphere checks that calcd. from argon and both agree with the accepted value of N , the blue of the sky must be due to light reflected from the mols. of the air rather than from suspended particles of liquid or solid. FARRINGTON DANIELS

The specific action of polarized light. II. FRITZ WEIGERT. *Ann. Physik* 63, 681-725(1920).—W. has studied, with improved methods, the action of polarized light on photo-chlorides in gelatin. Linearly and circularly polarized light of equal intensity produces differences in the color tints. The photosensitive system is dichromatic only if the electric vector of the exciting ray has a component in the plane of the system. Dichromatism is positive if the ray vibrating in the elec. direction is absorbed less strongly than that vibrating in the magnetic direction. Quant. measurements of dichromatism show that it is a sp. property. Time is an important factor. Exposures of 0.04 second were sufficient to give positive effects. Bahinet's rule concerning the relation between dichromatism and double refraction holds only for the red and blue. Weigert describes a new app. for measuring dichromatism based on the half-shadow principle, which is accurate to 0.1%. FARRINGTON DANIELS

Optically minimal particles. MARIE ANNA SCHIRMANN. Uppsala-Wien. *Jahrb. Radiat. Elektronik* 18, 22-78(1921).—A complete report including bibliography. The exptl. work described includes the color, intensity and polarization of lateral radiation from disperse systems and single particles; the dispersion of the polarization and the polychroism of spherical and non-spherical particles; the color, absorption, double

refraction and pleochroism of the transmitted radiation from disperse systems and single particles; the electro- and magneto-optic effects of disperse systems. The facts detd. are compared with the present status of the theory.

G. L. WENDE

The chromogenetic properties of sulfur and certain other elements. OLIVER C. M. DAVIS AND FREDERIC WM. RIXON. University of Bristol. *Phil. Mag.* [6] 42, 259-62(1921).—A comparison is drawn between the color of the corresponding binary compds. of O and S. The view is expressed that possibly color is in a measure dependent on the energy of association, more particularly with that energy left unabsorbed, the residual energy. In a table of 21 oxides and sulfides of various elements it is shown that the oxides having heats of formation above 70 cal. are colorless, while the limit of color of sulfides is in the neighborhood of 40.

S. C. LIND

The present position of the wave theory of light. R. A. HOUSTOUN. *Nature* 108, 61-4(1921).—A discourse.

W. H. ROSS

Bohr's theory of light emission. A. SOMMERFELD. *Jahrb. Radioakt. Elektronik* 17, 417-29(1921).—A reply to J. Stark (cf. *C. A.* 15, 2788). S. points out that most of Stark's objections are unjustified, except those which deal with the fundamental principles, and those are the general difficulties of the quanta theory.

E. FISCHER

The explanation of the continuous absorption and emission spectra of atoms by Bohr's theory. R. LAOENBURG. *Jahrb. Radioakt. Elektronik* 17, 430-4(1921).—A reply to J. Stark (cf. *C. A.* 15, 2788). The continuous spectrum is caused by the "free" electrons which are sep'd. from the electron shells of the atom, but still in their sphere of attraction; because of the various kinetic energies which they carry, they cause a continuous spectrum; but also these electrons follow Bohr's axiom $E_1 - E_2 = h\nu$.

E. FISCHER

The action of the Planck oscillator on the spectral energy distribution of radiation. ERICH KRETSCHMANN. *Ann. Physik* 65, 310-34(1921).—Although Bohr's atom model has had extraordinary success in explaining radiation phenomena, it still leaves the details of emission and absorption processes in the dark. The fact that only the classical model of an electromagnetic radiator, the quasi-elastically bound elementary charge or Planck oscillator, leads directly to a source of monochromatic electromagnetic radiation is justification for the present investigation, which, by means of a new form of integral of the oscillator equation, leads to the conclusion that in a stationary radiation field every oscillator augments the radiating intensity of its natural frequency in a measure which is proportional directly to the intensity of radiation and inversely to the frequency of the oscillator.

WILLIAM F. MCGERS

Critical potentials and band spectra of nitrogen. LEON AND EUGENE BLOCH. *Compt. rend.* 173, 225-7(1921).—The minimum potential difference through which an electron must fall to acquire sufficient energy to ionize an atom by collision is called the *ionisation potential*. If, instead of ionization, the impact causes only radiation of energy, the corresponding potential difference is called the *resonance potential*. The authors photographed the spectra of bombarded N contained at low pressure (about 0.04 mm. of Hg) in a glass bulb fitted with brass anode and hot filament cathode. A fluorite lens set in the side of the bulb transmited the ultra-violet. As the potential difference across the tube was increased and the resonance value for a particular spectrum was passed, this spectrum was radiated from a point near the anode. With increase of voltage the radiating region moved toward the cathode. The *resonance potential* of the positive band spectrum (Deslandres' second group) was found to be 12 volts; that corresponding to the negative band spectrum (only line 3914 was studied) was found to be 21.5 ± 0.5 volts. The generally accepted value of the *ionisation potential* is 18 volts. The authors attribute the positive spectrum to the neutral mol. and the negative spectrum to the mol. which has lost one electron.

HARRY CLARK

The magnetic separation of the fine-structure components of the lines of the helium spark spectrum. H. M. HANSEN AND J. C. JACOBSEN. *Kgl. Danske Videnskab. Selskab., Mathefys. Medd.* 3, No. 11, 25 pp.(1921).—The Bohr-Sommerfeld theory of hydrogen-like spectral lines, as applied to the Zeeman effect, indicates that each fine-structure component should be split into a normal Zeeman triplet, uninfluenced by other components. This theory has not been tested quant., since in previous work with H, only the magnetic splitting of the line as a whole was observed, and the results of different observers have been contradictory. The discrepancies are due probably to the superimposed effect of the elec. field, Bohr having shown that for H this effect is very large. The authors use the "4888" enhanced line of He, since this gives a more open fine structure and is also less susceptible to elec. effects. For work in a magnetic field it was necessary to design a special form of *spectral tube*, with large flat parallel electrodes, 6 to 7 mm. apart. Photographs were taken with plane grating, an echelon spectroscope, and a Lummer plate, all of high resolving power. The more important photographic results are reproduced in the article. Although the exptl. difficulties were found very great, some fairly definite data were obtained and the results thus far, for a field of about 6000 gauss, are, within limits of error, in agreement with theory, both as regards the state of polarization, and the position of the lines. For strong fields deviations from the simple theory appear, but these may be attributed to the disturbing elec. field, which accompanies a strong magnetic field. It is definitely proved that the 2 strongest fine-structure components of the 4888 line give an entirely different Zeeman splitting from that shown by ordinary visible series doublets such as the D lines. The work will be continued with the aid of photometric measurements. R. T. B.

The effects of violent molecular collisions in interference. G. GOUV. *J. Phys. Radium* 1, 3-11(1920).—A mathematical discussion showing that this explanation is inadequate for spectral diversity. G. L. WENDT

Absorption and series spectra of lead. J. C. MCLENNAN AND R. V. ZUMSTEIN. Toronto. *Trans. Roy. Soc. Canada* 14, Sect. III, 9-17(1920); cf. *C. A.* 14, 2584.—The absorption spectrum of non-luminous Pb vapor was obtained by using a tube of opaque fused quartz into whose ends were sealed 2 plates of plane-parallel clear fused quartz, and which was heated in an elec. furnace provided with a coil of stout nichrome wire. Marked absorption lines were found at 2833, 2170, 2053.83 Å., faint absorption at 2022.64, 2139 (probably due to Zn), 2288 (probably due to Cd). Suggestions are made for grouping certain prominent wave lengths of the Pb spectrum into a principal, 2 subordinate, and a combination series. A. T. CAMERON

The spectra of the alkaline earth fluorides and their relation to each other. SENGHAMOY DATTA. *Proc. Roy. Soc.* 99A, 436-55(1921).—The object of this investigation was to det. what relations exist among the band spectra of similar compds. The fluorides of the alk. earths were taken. Observations were made with a concave grating. Negatives for measurements were prep'd. in second order; those for reproduction in first order, and subsequently enlarged. The elec. arc between C poles was used. Na_2CO_3 mixed with the compds. examd. gave a "flame," having low order of temp. MgF_2 gives 3 groups of bands in the ultraviolet. CaF_2 shows 7 groups. Five are in the visible spectrum. Four new series were found in the ultraviolet. SrF_2 shows 11 groups. One in the visible region and 2 in the ultraviolet are new. BaF_2 shows 4 groups of bands in the visible region, all previously known. A relation between the homologous series has been expressed by empirical equations, with consts. of the series equations and the mol. wts. and the mol. numbers of the respective compds. I. D. R.

The arc and spark spectra of alkalies, alkaline earths and earths. R. SEIDLINGER AND D. THAER. *Ann. Physik* 65, 423-48(1921).—Only recently have attempts been made to associate different spectra with the elec. charges of the radiating particles or

the corresponding exciting potentials. The theories of Stark, Lenard and Sommerfeld are at variance in many points and it is the object of this investigation to test the "shift principle" and to det. qual., by expt., the order in which spectral lines appear with increasing velocity of cathode rays used to excite the radiations. Spectrograms were obtained of Li, Na, K, Mg, Ca, Zn, Hg, and Al which are representative of the first 3 columns of the periodic system. The discharge in the vicinity of the metal cathode was sharply focused on the slit set perpendicular to the cathode surface and photometric measurements were made on the spectral lines throughout their length. Close to the cathode is the so-called negative glow, sepd. from the positive column by the Faraday dark space. In general the spark spectra show max. intensity in the negative glow and not at all in the positive column, while the arc lines have their max. intensity in the latter region. The shift principle is verified for the alkalies, alkaline earths and earths inasmuch as all the lines of these elements can be arranged in two groups of small and large exciting energy. The energy required to excite the arc lines of these elements increases in the order: alkalies, alkaline earths, earths, and for the same element increasing energy calls forth groups of lines in the following order: Bergmann series, principle series, 2nd subordinate series, 1st subordinate series, singlet series, spark lines. W. F. M.

The stationary H and K lines of calcium in stellar atmospheres. MEGH NAD SAHA. *Nature* 107, 488-9(1921).—Certain stars having variable radial velocity show the H and K lines unaffected, suggesting that the gas giving rise to these lines is located in the space surrounding the system. Ca has been observed at a higher level than any other gas in the solar atm. The H and K lines are the resonance lines of Ca which has lost one electron, and atoms in that state are in the condition to absorb energy of the wave length of max. intensity in the solar spectrum. For this reason it is possible that radiation pressure may be able to overcome gravity and drive these atoms to great distances from the star's surface. The resonance lines of other elements are not so favorably situated as those of Ca, either for observation or with respect to the max. of radiation, which accounts for the fact that no other stationary lines have been found. [Stationary D lines were announced by Heger (*Pub. Astron. Soc. Pacific* 31, 304(1919).—Abstractor.] K. BURNS

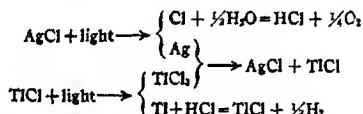
The spectrum of fluorine. WILLIAM R. SMYTHE. *Astrophys. J.* 54, 133-9(1921).—By a method due to Mather and others F was prep'd. by the electrolysis of fused KHF_4 , and purified by passing through Na_3F_2 and a freezing trap. The pump was protected by a charcoal trap. The gas flowed constantly through the sparking chamber and it was of such purity that the spectra of other elements were very weak or absent. The discharge passed between gold electrodes. A fluorite window permitted the photography of the ultra-violet region of the spectrum. Both a quartz spectrograph and a 50-cm. concave grating were used to photograph the spectrum. The only F lines found were 10 in the red; these are tabulated to the nearest 0.1 Å. An impurity which was supposed to be CF_4 was observed following a flare back from the charcoal chamber. The approx. positions of nine heads of bands between $\lambda 4829$ and $\lambda 6625$ were observed in this spectrum. K. BURNS

The radiation theory of thermal reactions. W. C. M. LEWIS AND A. MCKNOWN. Univ. Liverpool. *J. Am. Chem. Soc.* 43, 1288-1306(1921).—A theoretical and mathematical paper, in which by making use of the concept of continuous absorption of radiation by an oscillator (i. e., Planck's second formulation of the quantum hypothesis), an expression has been obtained for the velocity of a unimol. reaction in a gaseous system, on the basis of the radiation hypothesis of thermal reactions. By considering reversible reactions of the dissoc. type, an expression for the equil. const. has been obtained. Recent criticisms of the radiation hypothesis have been considered and it is believed that these have been met. H. JERMAN CASSIDON

A new effect of radiation. F. WEIGERT. *Z. physik* 5, 410-27(1921); cf. *C. A.* 12, 1727; 13, 1185; 14, 1931, 3595; 15, 1453.—W. investigates the directional effects of linearly polarized radiation on cyanine in collodion. The dependence on O pressure already observed for the bleaching effect of light is found to hold in the same degree for these effects. They are both diminished by the presence of O. The change of the dichroism with time is different from that of the bleaching effect, as the former shows a max. Its abs. value is always much less than that of the extinction change. In this respect these phenomena are different from the analogous effects in photochlorides. The total quantity of light absorbed by the dyestuff-collodion layer is not a measure of the time course of the photochemical and directional effects. The sensitivity of a freshly prep'd. layer decreases continuously during the illumination. The effect of illumination with a definite color is to make the dichroism for that color change most rapidly at first. The selective absorption for yellow does not become effective at once. The effect is as though there were a weak absorption, without a max., superimposed on the selective effect, which was the cause of the color sensitivity. In spite of chem. differences photochlorides behave very similarly to dyestuff-collodion systems.

F. C. HOYT

The photolysis of water. EMIL BAUR AND A. REBEMANN. *Helvetica Chim. Acta* 4, 256-62(1921).—Potential measurements of polarized electrodes indicate that certain light-sensitive dyes bring about decompr. of water in the light. A series of expts. designed to prove this is described. Positive results were not obtained. A differential tensimeter failed to give any gas evolution when filled with uranium salts, eosin, rhodamine, etc., and exposed to light. Precautions to prevent supersatn. were taken. Sufficient time was allowed to obtain equil. It was concluded that continuous photolysis of water can occur only if the system excludes the recombination of the H and O. Special systems were tried in which it was hoped to prevent the reverse reaction by secondary reactions but no positive results were obtained. The following system gave negative results:



A study of the two reactions separately showed that only traces of O could be obtained by the action of a quartz Hg lamp on AgCl in water and that the TiCl was not sensitive in the presence of acids. Photochem. reactions are rare because the reversal in the dark or secondary reactions prevent detection.

FARRINGTON DANIELS

Interaction of oxalic acid with iodic acid. III. Influence of sunlight (LEMOINE) 2. A simple device for making crystal-structure models (SPANGENBERG) 1. Theory of illuminants (SCHROETER) 4. Color and optical activity in organic compounds (LONGOBARDI) 10.

4—ELECTROCHEMISTRY

COLIN G. FINE

Recent progresses in electrometallurgy. C. F. BONINI. *Ann. chim. sci. ind.* 37, 132(1921).—A review.

E. FIERTZ

Electric reduction of iron ores. H. A. DE FRIES. *Chem. Met. Eng.* 25, 193-4(1921).—The comparative merits of the shaft and pit furnaces for the elec. reduction

of some ores are discussed. If lumpy ore and sintered concentrates are available, a large unit plant is desired, the demands of the central station are strict, and capital expenditure is of secondary nature, the elec. shaft furnace should be employed. If, however, only crude concentrates are available, or the plant depends upon a varying ore supply, no objections being raised against single-phase loads, and capital expenditure has to be limited, then the pit furnace apparently possesses considerable advantages over the shaft type.

W. E. RUDER

Superheats in the electric furnace. GEO. K. ELLIOTT. *Foundry* 49, 714-19(1921).—The cupola-elec. furnace duplexing process has been in successful operation in progressive foundries for about 4 yrs., the largest passing over 200 tons of gray iron through the elec. furnace every 24 hrs. Metal from the cupola usually ranges from 1300 to 1465°. This temp. may drop 50-150° by the time it reaches the mold. To make a good casting, particularly in the case of strong irons contg. low P, fluidity is necessary, and the most powerful factor for this is superheat. With an elec. furnace, cupola iron can be raised from 1300° to 1500° with incidental refining, on about 200 kw.-hrs. per ton, varying with the size of furnace. A thorough deoxidation and desulfurization is recommended. With a basic furnace, and proper condition in furnace and slag, a reduction of S from 0.156 down to 0.079 in 30 min. and to 0.014% in 60 min., is obtained with a single slag. It is believed that if S is below 0.07 it cannot be considered dangerous in any ordinary gray iron casting. S reduction under 0.05 is needed only under special conditions, and its value is largely speculative. An indirect benefit from reduced S is a saving in Mn. C can readily be controlled while the metal is in the elec. furnace. P cannot be reduced except by an entirely uneconomical process, or by diln. with steel. In the U. S. duplexing costs \$8-\$15 above the cost of ordinary cupola Fe. Duplexing is eligible wherever high quality or strong insurance against defective castings is desired. It should not be looked upon as a foundry cure-all, and satisfactory results are obtained only by careful and intelligent supervision.

W. E. RUDER

Electric furnace in steel manufacture. J. A. EDGERTON. *Commonwealth Engineer* 9, 44-7(1921).—A six-ton three-phase arc furnace has been installed at the Victoria Iron Rolling Mills, West Melbourne. The normal input is 1500 kw. The electrodes are 17 inch carbons having a normal carrying capacity of 8,670 amperes. The power factor averages about 87%. The furnace shell is 12 ft. in diam. The bottom and sides of the furnace are lined with 2 courses of 9-inch magnesite brick. A little fine dry magnesite cement is used between joints. The roof is of silica brick. In laying these a concrete template was used and cardboard pieces were placed between bricks to allow for expansion. The amt. of steel scrap charged usually varies from 6.5 to 7.5 tons. On the bottom of the furnace are thrown 800 lbs. of limestone. With very clean scrap of high C%, 200 to 300 lbs. of Fe ore and mill scale are added. (The make of the furnace is not given.)

C. G. F.

Electric furnace for silver, gold, and metals of low melting point. JONAS HERKENRATH. *Chem. Met. Eng.* 25, 454-8(1921).—The essential requirements for the successful melting of Ag are quick heating, no local over-heating, efficient temp. control, exclusion of air, and mechanical provisions to allow of easy access to the bath for working and quick pouring. The Rennerfelt furnace has given good results in several installations. The Baily pit furnace is also in successful use, but its power consumption is quite high, owing to the indirect heating of the metal in crucibles. Induction types are unsuitable, on account of the high elec. cond. of the metal. The high frequency furnace has given excellent results in small installations, but there are still some mechanical difficulties to be overcome before this type will be entirely satisfactory. It is more satisfactory for Au and Au-Pt alloys. In a 6" crucible with a net vol. of 58 cu. in. 37 lbs. of Au can be melted in 8 min. at a rate of 14 lbs. per kw.-hr. in a high frequency

furnace. For metals such as Zn, Sn or Pb, resistance radiating furnaces with accurate control are the best.

W. E. RUDER

Melting fine and sterling silver by electricity. H. A. DE FRINS. *Chem. Met. Eng.* 25, 507-8(1921).—For casting Ag into bars for remelting a temp. of 1040-95° is sufficient. For rolling stock or castings, however, such metal would be too brittle. Such metal should be cast at 1295°-305° if horizontal molds are used, or at about 1205° if vertical molds are used. Any chilling between furnace and molds should be guarded against, as a difference of 90° will cause trouble. During melting the Ag should not be stirred or rocked. The great susceptibility of Ag for gases gives the elec. furnace a great advantage. A nearly neutral or slightly reducing atm. is best. The metal travel from spout to mold should be as short as possible. The small amt. of impurities that may be present is removed by slagging or cupelling. The latter method is usually employed. The indirect arc furnace or the high frequency types of elec. furnace are the best for Ag melting. Tests on each type show a power consumption of about 320 kw. hrs. per ton of Ag melted. The cost of melting in a 10,000 oz. Rennerfelt furnace is given as \$0.7725 per 1000 oz. It was found that elec.-method Ag was much finer grained and easier to roll than crucible Ag. It gave 100% sound forgings against 15% from crucible Ag, and an extreme long draw in spinning was 100% perfect, while crucible Ag failed completely. The introduction of a block of Fe into the molten silver as an O₂ absorber and heat equalizer was found to be decidedly advantageous. Also in *Brass World* 17, 291(1921); and *Trans. Am. Electrochem. Soc.* 40, preprint(1921). W. E. R.

Recent developments in electric furnaces of the muffled arc type. H. A. WINHE. *Trans. Am. Electrochem. Soc.* 40, advance copy(1921); cf. *C. A.* 15, 2794.—For smaller units, melting 1500 lbs. per hr. or less a new type of furnace has been developed which uses the smothered-arc principle, applied in a more compact form. The energy is introduced through the roof by means of three electrodes which rest in disked carbon blocks, the contact being made through crushed graphite. These blocks are adjacent to the wide walls, and are protected by a layer of carborundum cement. They rest upon 3 radial graphite cross electrodes which lie between the first and third courses of brick in the bottom, and are connected at the center to form a V. Three-phase power at 60 v. is used. The power input is regulated by small motors on the electrodes, automatically controlled. A test run for several months on brass on a 24 hr. per day basis showed a power consumption of 250-300 kw.-hr. per ton. With 9 hr. per day operation this rose to 325-375 kw.-hrs. per ton. In melting a 30% Zn alloy the total loss by wt. including spillings, etc., was only 1.14%. A smaller furnace designed to take a standard No. 20 crucible is also described. This furnace will melt 100-125 lbs. of brass per hr. with 35-40 kw.-hrs. per 100 lbs. on continuous operation. The advantages of small space for heating elements, low metal losses, reducing or neutral atm. and small load fluctuations are claimed.

W. E. RUDER

Electric-furnace purification of zirkite. J. G. THOMPSON. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—Zirkite ore was treated in elec. furnaces to remove the Fe, Si, Ti, and other impurities usually associated with it. It was found that the temp. required was too high for a resistance furnace. With an arc furnace 90-95% of the Si could be removed by heating the ore to 2220° or higher, provided coke was added in just the proper amt. to transform only the Si to carbide. The existence of stable double carbides of Si and Zr, or of solns. of SiC in solid ZrC, is suggested as an explanation of the incomplete removal of the Si when an excess of C is present. The further treatment of the ore with Cl or PH₃, to remove the Fe is suggested.

W. E. RUDER

Rotary electric furnace shows marked advantages. ALAN D. DAUCH. *Elec. World* 78, 565-6(1921).—A circular elec. furnace with a moving annular hearth has been designed for heat treating, annealing, and carbonizing. The hearth rotates on a series

of 20 roller bearings. The clearance space between the hearth and the furnace side walls is closed by sand seals. Charging and discharging doors are adjacent with a baffle wall extending across the heating chamber between the two doors to prevent the heated pieces being chilled when cold material is charged. The hearth is driven by an elec. motor and has 6 speeds varying from 1 revolution in 30 min to 1 revolution in 75 min. The heating elements are Ni-Cr ribbon mounted on the inner and outer walls of the furnace. These heating elements are in two sets; the first, the main or heating zone, is run at a temp. of 800° and extends $\frac{2}{3}$ of the distance around, starting at the charging door; the second, or soaking zone, operates at 830° . The temp. of each section is automatically controlled and recorded. The steel charged is heated and soaked at the rate of 166 kw.-hrs. per ton. The charge per hr. is approx. 3000 lbs. of automobile parts varying in size from 3 to 180 lbs. each. The advantages of this furnace over the box-type oil-fired furnace which it displaced are: the entire elimination of the distortion of long parts (axles); scaling virtually eliminated; increased hardness and more uniform strength and other physical properties; labor for handling the same number of parts reduced from 6 to 3 men.

LOUIS JORDON

The electrolytic chlorine-alkali decomposition and the apparatus employed in it. CARL TÜSCHEN. *Chem. App.* 8, 135-7 (1921); 6 cuts.—A brief description of the Siemens-Billster cell, which on a large scale has given a current efficiency of 94.7% with only 1.17% CO₂ in the Cl gas. It has a bath tension of 3.7-4.0 v. The graphite anodes and the diaphragms last 1.8-2.0 yrs. The caustic soln. contains 125-150 g. per l. NaOH.

J. H. MOORE

The electrolytic oxidation of hydrochloric acid to perchloric acid. H. M. GOODWIN AND E. C. WALKER, 3RD. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—Expts. are described for the production of perchloric acid by electrolysis of HCl. The yield depends upon: the duration of electrolysis, c. d. on the anode, concn. of HCl, temp. of the cell, and the anode material. The app. used consists of two concentric cylinders; the inner, a Pt tube 22 cm. long, 0.55 cm. diam., serves as cathode. The Pt tube passes through a rubber stopper, closing the end of the Cu cylinder. Parts of Cu subjected to Cl fumes are coated with paraffin. The temp. of the cell is regulated by the passage of running water through the anode and around the cathode. At completion of the electrolysis, Cl is removed from the electrolyte by shaking with Hg, filtering off the Hg₂Cl₄ and detg. chloride-, chlorate- and perchlorate-Cl. Total acidity is detd. by titration with 0.1 N NaOH, phenolphthalein being used as indicator, chloride Cl is detd. by the usual volumetric method, and Cl by reduction with FeSO₄, boiling and joint pptn. of chloride-chlorate-Cl. Perchloric acid is then detd. by difference. The cell finally adopted for com. production consists of a rectangular trough flared at the top. It consists of sheet silver (76 X 35.5 X 0.013 cm.) serving as cathode and sheet lead (12.7 X 41 X 0.0038 cm.) suspended in the center serving as anode. The trough is reinforced and a Ag outlet tube is welded to the bottom. Cooling water sprays the side. All Cu parts are protected by bakelite. The electrolyzed liquor runs into two fused silica dishes arranged in cascade. The liquor is evapd. to a 60% concn. Sr, Zn, Cu, Mn, Ni, Co, Fe'', Fe''', Sn, Bi, Au, Be, and U salts have been prep'd., which are very sol. in water and most of them are very hygroscopic, and quite stable. A bibliography is given.

W. H. BOYNTON

Graphic control of electrolytic processes. B. G. WORTH. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—In the case of KClO₄, the end product depends as much on the relations of the ions in the soln., and their soln. pressures, bath temp., etc., as on essentially electrolytic effects. Fixed conditions are maintained by use of a graph and high yields depend upon the relation between three factors. *A* and *B* represent concns. of two compds. and *T*, temp. A certain numerical relation must exist between *A* and *B*.

A is incapable of direct control (being the result of the establishment of equil.), but *B* is controllable by addition agents. "Proper *B*" (*PB*) is the computation for *B* when *A* is known. Curves show that whenever *B* advances or recedes beyond a certain point remedial measures should be taken.

W. H. BOYNTON

Electrolytic production of sodium perborate. P. C. ALSGAARD. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—A. describes in detail the work of Arndt and of Valeur on the electrolytic production of NaBO_3 . In some preliminary expts. the electrolyte contained Na_2CO_3 , NaOH , and borax at moderately low temps. Addition of small amt. of different substances showed water-glass alone of these favorable to an increased yield of NaBO_3 . Even at 0° the electrolyte becomes highly supersatd. with NaBO_3 and when crystn. starts several days may be required to obtain complete crystn. Exptl. results are tabulated. The best results were obtained with an electrolyte of the following compn. per l.: 45 g. borax, 130 g. NaHCO_3 , 2 g. K_2CrO_4 , and 2 g. water-glass.

W. H. BOYNTON

The structure and properties of alternately electrodeposited metals. WILLIAM BLUM. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—If relatively thin layers of Ni are interposed during the deposition of Cu, the deposit has a much higher tensile strength than has pure Cu deposited under similar conditions. It is shown that this effect is due to the influence of the Ni layers in arresting the growth of the Cu crystals and keeping them fine grained. The same effect is observed with layers of Cu and Ag, or even with layers of Cu from the sulfate and cyanide solns., resp. The principle has been applied in the electrolytic reproduction of engraved plates. Also in *Chem. Met. Eng.* 25, 961-3 (1921).

L. C. K.

The electrodeposition of lead-tin alloys. WILLIAM BLUM AND H. E. HARING. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—It is possible to deposit from fluoborate solns. alloys of Pb and Sn, which are finer grained than either of the metals deposited under similar conditions. Pb and Sn can each displace the other from such solns., until equil. is reached, at which the two metals have the same potential. During continued electrolysis with Pb-Sn anodes, of solns. contg. Pb and Sn, the ratio of the metals in the deposit always tends to approach that in the equil. soln. The process is used on a com. scale by the Navy Department.

L. C. K.

Nickel plating aluminium. L. GUILLET AND M. GASNIER. *Rev. metal.* 17, 351-8 (1920).—Cf. *C. A.* 14, 2760.

S. L. C.

Recent applications of the Cottrell process. R. B. HESSON, P. E. LANDOLT AND A. A. HINDROP. *Eng. Mining J.* 112, 446-9 (1921).—Installations of this process for the recovery of valuable metallic particles have recently been made at the plants of the National Lead Company, and the Williams-Harvey Corp. Metallic losses of Zn, Sn, and Pb are prevented. A description of the mechanical and elec. features is given. Performance tests on the National Lead installation showed a recovery of 97% of the suspended matter which consisted of 40-50% Zn, 15-20% Pb and 15-20% Sn, all as oxides. Gases at 345° and 12,000 cu. ft. per min. are treated. Total cost of installation was \$30,000, and annual operating charges are about \$10,500. Expected recoveries will be 450,000 lbs. of dust at a value of about \$18,000, netting 20-30% on the investment. The other plant cost \$125,000 complete, and returns from dust are at the rate of \$100,000 per year or \$70,000 above all expenses. A bibliography is attached.

W. E. RUDER

Theory of illuminants dependent on (electro-) luminescence. F. SCHONVIEZ. Berlin. *Elektrotechnik u. Maschinenbau* 38, 237-42, 251-7 (1920).—This paper undertakes a short discussion of the present importance of electroluminescence lamps, of their internal processes in the light of recent theories of atomic structure, and of the possible development of this type of lamp, especially in regard to efficiency. The present

type of incandescent filament lamp probably will not approach the max. theoretical efficiency of a black body (9.8 Hefner candles per watt at 6000 to 7000° K.) more nearly than it does now unless new materials extremely resistant to high temp. are found. With the pressure arc it is possible to attain the theoretically optimum temp. but its technical realization is prevented by the lack of simplicity in construction and operation of pressure arc lamps. In monochromatic luminescence lamps the max. theoretical efficiency is 55-72.5 Hefner candles per watt. The following efficiencies for luminescence lamps have been realized: He glow discharge, 0.34; N glow discharge, 0.67; He vacuum arc, 0.63; Ne glow discharge, 1.45; Ne vacuum arc, 2.00; Hg vacuum arc, 2.63; Hg high pressure arc, 4.80; Hg-Cd high pressures arc, 6.25; Na-Ca "effect" arc, 11.36; Hg + salt vapor arc lamps (Nernst), 6.25 Hefner candles per watt. For signal lamps the luminescent gas column allows a higher signal frequency than can be attained with an incandescent filament. The low threshold current of the Ne lamp, for example, favors its application as an indicator in testing insulation, cables, and condensers. The temp. of the radiating mols. in the high-pressure Hg vapor lamp has been estd. as 18000° K. The kinetic energy of positive ions in N at 1 mm. and under a cathode fall of 200 v. corresponds to a temp. of 58000° K. Light emission also results from the recombination of ions. The future development of luminescent light sources will include the realization of lower operating potentials, high gas or vapor densities, and the conversion of the kinetic energy of the positive ions into temp. radiation by using regions of high energy density. From theoretical and exptl. considerations efficiencies of from 36 to 51 Hefner candles per watt (about 0.03 to 0.02 w. p. c.) are physically possible. There is a possibility of utilizing ultra-violet radiation to excite fluorescence, although this effect is rarely exhibited by gaseous substances.

D. MACRAE

Thermic accumulation of electrical energy. G. DURANDO. *Electrotecnica* 8, 94 (Feb. 15, 1921); *Science Abstracts*, 24B, 248-9.—Fused salts or rods of C, Si and B compds. are employed as heat-generating resistances. The heat of soln. of certain salts or the heat of fusion of others is utilized to accumulate heat up to a temp. of 600°. For temps. up to 1500° one of 3 substances is employed (the compn. of which is not disclosed) having a sp. heat equal to, or slightly higher than, that of water. Cork, or a substance composed mostly of cork and called "expansit," is used as a thermal insulating substance for low temp. For middle and high temps., a conglomerate of cork and fossil flour, such as porosite and diatomite, was employed. Better results were obtained with a material formed of the same substances but in different proportions and named by the author "Cellular D." The most favorable dimension of the cavities was 3 mm. This substance possesses a thermal resistance 20% higher than porosite and diatomite. A "differential accumulator" consists of two or more concentric heat-accumulating elements, sep'd. by heat-insulating substances. The central element only is heated by electricity and is, therefore, subjected to the highest temp. The heat which passes through the insulator surrounding it is accumulated in the second heat-accumulating element which surrounds this insulator. In this way the heat is accumulated at lower and lower temps. as it proceeds from the central to the outside elements. An external insulating wall closes the accumulator. By using a sufficient number of concentric elements the efficiency of the app. can reach 99%. These accumulators may be applied in a number of cases, such as drying stoves, domestic heating, electrothermic kitchen cookers, steam generators, etc. The accumulators are especially adapted for cooking purposes, proving more efficacious than a gas flame.

L. C. K.

Modern power (mercury arc and tungar) rectifiers. R. G. CRIVELLI. *Commonwealth Engineer* 9, 40-3 (1921).—A review. 7 illus.

C. G. F.

Storage battery. L. LYNDON. U. S. 1,388,656, Aug. 23. Structural features.

Storage battery electrodes. V. C. STANLEY. U. S. 1,388,530, Aug. 23. Structural features.

Mold for storage-battery grids. L. B. HILLS. U. S. 1,387,928, Aug. 16. Structural features.

Dry-cell electric battery. H. W. JONES. U. S. 1,387,928, Aug. 16. A hollow Zn electrode is used, the edges of which are autogenously welded together.

Electrolyzing salt solutions. A. H. HOOKER. U. S. 1,388,466, Aug. 23. In the electrolysis of salt soln. to produce NaOH in diaphragm cells, an aq. electrolyte carrying solid salt is supplied to the electrolytic cell, in order to maintain the electrolyte approx. satd. at working temp.

Ammonia by electrolytic reduction of nitrates. H. BLUMENBERG, JR. U. S. 1,388,448, Aug. 23. An aq. soln. of a nitrate such as NaNO₃, and Ca(OH)₂, is electrolytically reduced to nitrite, which is further reduced by the H produced, to form NH₃, and hydroxide of the metal of the nitrate used.

Electrolytic apparatus adapted for treating salt solutions in diaphragm cells. T. L. B. LYSTER and K. E. STUART. U. S. 1,388,474, Aug. 23. Provisions are made for circulating the electrolyte and for introducing it to the electrolytic cell under a constant head.

Electrolytic cell adapted for stirring and circulating the electrolyte. C. J. THATCHER. U. S. 1,388,216, Aug. 23. Structural features.

Electrolytic diaphragms. W. E. GREENAWALT. U. S. 1,387,705, Aug. 16. Diaphragms adapted for use in electrolytic cells are formed of sections of porous material, such as burnt porous clay, united by rubber-covered metal rods filling adjacent grooves in the edges of superposed sections.

Metal diaphragms for electrolytic cells. R. PFEHRKRAZ. U. S. 1,388,754, Aug. 23. Metal diaphragms such as used in electrolytic cells are formed by electro-deposition of the metal, e. g., Ni, upon a foundation of textile fabric or other material which will be inert to the electrolyte of the cell in which the diaphragm is to be used.

Electroplating apparatus with a revolute drum. F. H. HARTZELL. U. S. 1,388,337, Aug. 23.

Electrolytic condensers. J. COULSON. U. S. 1,387,471, Aug. 16. Electrolytic condensers, lightning arresters, rectifiers, etc., are provided with an electrolyte comprising a 1% aq. soln. of NH₄ tartrate, which forms films on condenser plates used, such as Al or Mg.

5—PHOTOGRAPHY

LOUIS DERR

Desensitizing panchromatic plates. H. N. HOLLAND. *Bril. J. Phot.* 68, 271(1921).—When phenosafranine is used as a desensitizer, the stain on the plate is sometimes uneven, and occasionally a blue-violet tint will appear on drying a seemingly stainless plate. At present, for panchromatic plates the use of the usual green safe-light seems preferable to a desensitizing dye. L. DERR

Use of salts of tin for preserving developers. J. DESALME. *Bull. soc. franç. phot.* [3] 8, 192-3(1921).—Dissolve 5 g. SnCl₄ and 5 g. tartaric acid in 30 cc. hot water, dil. to 100 cc. and filter. This soln. added to 1000 cc. of diaminophenol developer preserves it from atm. oxidation a long time and permits the use of the rapidly oxidizing diaminophenol like other developers. L. DERR

Studies on development-fixing. L. J. BUNEL. *Bull. soc. franç. phot.* [3] 8, 193-4 (1921).—The bath recommended is diaminophenol 5 g., anhyd. Na₂SO₃ 30 g., acetone 90 cc., hypo 50 g., water 1000 cc. This compares favorably with the Lumière chloranol

bath (see following abstr.). Generous exposure is required. The substitution of caustic alkali for acetone failed to give satisfactory results.

L. DEINER

Simultaneous development and fixing. A. AND L. LUMIKER AND A. SZEWCZYZ. *Bull. soc. franç. phot.* [3] 8, 220-1(1921); cf. *C. A.* 15, 2041.—The Binzel bath (see preceding abstr.) keeps only 1 hr. after prepn. and has a marked tendency to dichroic fog. The following bath is recommended: *A*, water 400, chloranil 6, anhyd. Na_2CO_3 32; *B*, water 600, Na_3PO_4 100, hypo 40. Mix 2 of *A* with 1 of *B*. Not all emulsions require overexposure.

L. DEINER

Desensitizing autochrome plates before development. A. AND L. LUMIKER AND A. SZEWCZYZ. *Bull. soc. franç. phot.* [3] 8, 218-20(1921).—Aurantia, in 0.1% soln., is extremely effective. It is easily washed out and does not retard development. Picric acid is much less satisfactory.

L. DEINER

Investigations on curves of blackening. HANS ARENS. *Z. wiss. Phot.* 21, 29-36 (1921).—If measurements are made with a polarization photometer on a plate of varying opacity, a curve is obtained which shows how the light intensity necessary for a photometric match increases with the darkness of the plate. As the plate is less sensitive to light in the visible range than the eye, the curve for the true photographic light intensity lies above that detd. visually, and by a const. amt. The importance of this curve is shown in the case of negatives that have been changed in color transmission through intensifying, thinning or toning, for their relative intensity of light and dark will be quite different as recorded by the eye and photographically.

G. R. FONDA

Color photography. W. FRIESK-GREENE. U. S. 1,383,460, July 5. A 2-color process is carried out by prep. pairs of negatives on successive portions of a light-sensitive material, using alternately white light and a flavazine or similarly colored screen. Positives are prep'd. from the negatives and the positive from the white-light negative is used to give a blue-green color and the other positive a reddish shade. The process is especially intended for use in the production of cinematographic films.

Color-sensitizing photographic plates. W. FRIESK-GREENE. U. S. 1,383,620, July 5. A mixt. for color-sensitization of photographic plates is formed of pinacyanol 2 grains, pinaverdol 6 grains, pinachrome 2 grains, flavazine 4 grains, NH_4OH (0.880 sp. gr.) 4 oz. and H_2O 65 pints. Plates sensitized with this mixt. are especially adapted for use in two-color methods.

Matrices and color screens. I. KIRSAG. U. S. 1,383,819, July 5. A color screen integral with a moving picture film is prep'd. by first producing a matrix with the required fine lines with the aid of a one-row templet, printing from this on a dichromate-sensitized substratum, raising the protected parts and then selectively coloring the substratum with at least 2 colors.

Acetylcellulose composition. W. G. LINDSAY. U. S. 1,388,472, Aug. 23. A mixt. adapted for making photographic films is formed of acetylcellulose, borneol and other solvents or modifying agents.

6—INORGANIC CHEMISTRY

H. L. SCHLESINGER

The introduction of silicic acid into the nucleus of complex compounds. ROMBERT SCHWARZ AND HANS BAUSCH. *Ber.* 54, 802-13(1921).—Among the more credible theories regarding the constitution of the Al silicates is that of W. Vernadsky, namely, that they are hydrates or salts of complex aluminosilicic acids. To cast light on the problem of the constitution of the *silicates*, the authors have studied the reactions of Na_2SiO_4 with complex compds. of known constitution, namely, hexamminocobaltic

chloride, and chloropentamminocobaltic chloride. 1.25 g. Na_2SiO_3 in 50 cc. H_2O reacts with 2.5 g. $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}$ in 500 cc. H_2O to form *tetrasilicate-chloro-tetrammino-cobalt*, $[\text{Co}(\text{NH}_3)_5\text{Cl}(\text{Si}_4\text{O}_8)]$. When dry, this is a reddish violet, fine, non-cryst. powder. Heated at 120° it leaves marine-blue *cobaltous tetrasilicate*, CoSi_4O_8 . It does not react with H_2O or cold dil. HCl, but hot HCl decomposes it, setting free all the SiO_4 . Hot, strong NaOH soln. decomposes it with the separ. of Co(OH)_2 , which reaction was used in the quant. analysis of the compd. 50 cc. 2% soln. of Na_2SiO_3 and 2.5 g. $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}$ in 500 cc. H_2O react forming a yellow-orange ppt. of *silicate-tetrammino-cobaltic chloride*, $[\text{Co}(\text{NH}_3)_4(\text{Si}_4\text{O}_8)] \text{Cl}$, which can be freed from small amts. of adsorbed H_2O only at 105° and with accompanying decomprn. It is insol. in H_2O is decomposed by dil. mineral acids, and even slowly by warm AcOH, setting free SiO_4 . Heated, it decomposes according to the equation $[\text{Co}(\text{NH}_3)_4(\text{Si}_4\text{O}_8)] \text{Cl} = \text{CoSi}_4\text{O}_8 + 4\text{NH}_3 + \text{Cl}$. Inasmuch as this silicate-complex is a cation, silicates of it should exist under suitable conditions. The reaction between 2.5 g. $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}$ in 500 cc. H_2O and 2.5 g. Na_2SiO_3 in 50 cc. H_2O yields a yellow ppt. of *silicate-tetrammino-cobaltic silicate*, $[\text{Co}(\text{NH}_3)_4(\text{Si}_4\text{O}_8)]_2\text{SiO}_4$. This is the first synthetic silicate-silicate which has been prep'd., and may be of interest in the interpretation of many reactions of the natural Al silicates. This compd. is decomposed by acids. When decomposed by heat, the product is not a simple substance. It was impossible to effect a separ. of the Si within the nucleus from that in the SiO_4 anion. When the luteo-base, $[\text{Co}(\text{NH}_3)_5](\text{OH})_2$, was treated with a suspension in H_2O of dioxo-disiloxane, $\text{Si}_2\text{H}_2\text{O}_2$, there was formed the complex base, $[\text{Co}(\text{NH}_3)_4(\text{Si}_4\text{O}_8)]-\text{OH}$, in which case the Si has entered the nucleus instead of forming a silicate with the complex as the cation. These facts add probability to the theory that many of the Al silicates are not silicates, but silicate-compds. in which Si radicals are coördinatively bound to the Al along with aquo-, oxo- and other groups, forming complex nuclei. The above compds. can be prep'd. smoothly and free from by-products only by using cryst. Na_2SiO_3 and adhering strictly to the quautities and concns. specified in the article.

R. H. LOMBARD

Siliconhydrides X. Nitrogen-containing compounds. ALFRED STOCK AND KARL SOMMER. *Ber.* 54, 740-58 (1921); cf. *C. A.* 15, 2394.—The authors have studied the action of NH_3 on SiH_3Cl and SiH_2Cl_2 . These reactions give N derivs. of monosilane which contain the groups SiH_3 and SiH_2 , and many of which are volatile, simple mol. substances. These compds. form a new basis for the comparison of Si with C-chemistry. NH_3 reacts with an excess of SiH_3Cl gas quantitatively at room temp. to form *tri-monosilyl-amine*; $3\text{SiH}_3\text{Cl} + 4\text{NH}_3 = (\text{SiH}_3)_3\text{N} + 3\text{NH}_4\text{Cl}$. $(\text{SiH}_3)_3\text{N}$ is a mobile, colorless liquid, h. p. 52° . It is explosively spontaneously combustible in air, stable in the absence of air, and is decomposed by H_2O , yielding SiO_2 , NH_3 and H_2 . Its m. p. is -105.7° ; $d_{18}^{20} = 0.895$, and its vapor pressure is given by the equation, $\log p = (-1956.10/T) + 1.75 \log T - 0.00830 T + 7.20404$. Its vapor density corresponds to the formula $(\text{SiH}_3)_3\text{N}$. It does not form additive compds. with HCl or SiH_3Cl . Consequently salts like $(\text{CH}_3)_3\text{N}\cdot\text{HCl}$ and $(\text{CH}_3)_3\text{N}\cdot\text{HCl}$ do not exist, at least at ordinary temp. The reaction between an excess of NH_3 and SiH_2Cl_2 is complex. All the Cl forms NH_4Cl . At first $(\text{SiH}_2)_2\text{NH}$ gas is formed preponderantly, together with smaller amts. of $\text{SiH}_3(\text{NH})$ gas, and $(\text{SiH}_2)_2\text{N}$. The $(\text{SiH}_2)_2\text{NH}$ decomposes gradually according to the equation $(\text{SiH}_2)_2\text{NH} = \text{SiH}_4 + \text{SiH}_2(\text{NH})$. The $\text{SiH}_2(\text{NH})$ polymerizes rapidly to a solid, $[\text{SiH}_2(\text{NH})]_x$. To a less extent occurs, $\text{SiH}_2(\text{NH}) \rightarrow (\text{SiH}_2)_2\text{NH} \rightarrow (\text{SiH}_2)_3\text{N}$, each step being accompanied by the splitting off of NH_3 . Therefore, the final products of the reaction between excess NH_3 and SiH_2Cl_2 are NH_3 , SiH_4 , $[\text{SiH}_2(\text{NH})]_x$, and $(\text{SiH}_2)_3\text{N}$. SiH_2Cl_2 reacts with an excess of NH_3 to form $\text{SiH}_3(\text{NH})$; $\text{SiH}_2\text{Cl}_2 + 3\text{NH}_3 = \text{SiH}_3(\text{NH}) + 2\text{NH}_4\text{Cl}$. As above, the $\text{SiH}_3(\text{NH})$ polymerizes to $[\text{SiH}_3(\text{NH})]_x$, leaving only excess NH_3 in the gas space. Because of the formation of this solid product

the reaction between SiH_xCl_2 and excess NH_3 , does not proceed quantitatively. The polymer $[\text{SiH}_x(\text{NH})]_x$ is a white substance similar to silicic acid. It does not add HCl . It reacts with NaOH soln., and less rapidly with H_2O ; $\text{SiH}_x(\text{NH}) + 2\text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_4 + \text{NH}_3$. The f.-p. lowering of a C_4H_4 soln. of the polymer indicates that x is at least 7 or 8, but the solid form is probably even more highly polymerized. When the above Si-N compds. are treated with HCl gas, addition of HCl and salt formation does not occur, as in the case of amines, but SiH_3Cl is re-formed, together with NH_4Cl . Attention is called to a number of similarities between these N-compds. of Si and the O-compds. of Si previously studied by the authors. (C. A. 14, 1494.) Differences and similarities between the Si-N compds. and the analogous C-N compds. are also discussed. *The preparation of SiH_3Cl (b.p. -30°) and of SiH_3Cl_2 (b.p. 8°)*, which were used as starting substances in this research, is described.

R. H. LOMBARD

The ternary system ammonium chloride-manganous chloride-water. F. W. J. CLENDINNEN AND A. C. D. RIVERT. *J. Chem. Soc.* 119, 1329-39 (1921).—Considering it unlikely that working at 25° only (Foote and Saxton, *C. A.* 8, 3273) would show the exact type of this system, since $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ is not at this temp. a stable phase in pure water or in dil. NH_4Cl soln., the authors worked at 60° and have used the results obtained there to explain the 25° isotherm. The 60° isotherm shows 3 distinct curves in equil., resp., with 3 sets of mixed crystals, there being two gaps in the series of solids from pure NH_4Cl to pure $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$. The compn. of the hitherto accepted compd. $2\text{NH}_4\text{Cl} \cdot \text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ occurs in the intermediate series of mixed crystals. At any selected temp. a solid of this compn. can exist in equil. with one soln. only. Application of the term compd. to such a case is criticized. The 25° isotherm was also completely detd. and existence of mixed crystals richer in $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ than 2:1:2 made certain. It is pointed out that the term "compound" cannot be applied, strictly speaking, to the solid of compn. of a max. in a concn.-compn. curve. The compn. of a mixed crystal varies for some hours with the time for which it has been in contact with the soln. It is as if a supersatd. solid soln. formed first which then steadily rejects one of its constituents, the process being accompanied by fracture of the crystals. A. R. MIDDLETON

Absorption of oxides of nitrogen by nitric and sulfuric acids. A. SANOURCIE. *Compt. rend.* 172, 1573-6 (1921).—Equimol. proportions of NO and NO_2 act upon H_2SO_4 unlike a simple mixt. Through its high reaction velocity the small concn. of N_2O_4 present acts as a carrier, being reformed as fast as used. $\text{N}_2\text{O}_4 + 2\text{H}_2\text{SO}_4 = 2\text{HNO-SO}_4 + \text{H}_2\text{O}$ followed by $\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_4$. Absorption of this gas mixt. by HNO_3 , H_2O and alkalies proceeds by a similar mechanism.

A. R. M.

Ammoniacal silver carbonate. DERVIN AND OLMER. *Compt. rend.* 172, 1662-3 (1921).—Crystals of $\text{Ag}_2\text{CO}_3 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ were obtained by repeated evapns. in air of solns. of ammoniacal Ag_2O . When exposed to air the crystals lose H_2O and NH_3 leaving Ag_2CO_3 which retains the form of the original crystals. The crystals of amminocarbonate are blackened by sunlight.

A. R. M.

Studies on hypophosphorous acid. III. Reaction with mercuric chloride. A. D. MITCHELL. *J. Chem. Soc.* 119, 1266-77 (1921); cf. *C. A.* 15, 621.—The measurable velocity under similar conditions is almost the same for HgCl_2 as for I_2 , provided the concn. of the latter does not fall below 0.02 mol. nor that of HgCl_2 below 0.05 mol. The av. value of the velocity k for HgCl_2 was 134×10^{-4} as compared with 128×10^{-4} for I_2 . Strong, but not quite conclusive, evidence was obtained that the rapid reaction takes place between one mol. of HgCl_2 (and not of its ions or possible complexes) and two mols. of "active" hypophosphorous acid, the hypothetical H_3PO_2 , which suggests formation and rapid decompn. of an intermediate compd.

A. R. MIDDLETON

Investigations of zirconium with especial reference to the metal and oxide. J. W. MARDEN AND M. N. RICH. *Bur. Mines, Bull.* 186, 146 pp. (1921); cf. *C. A.* 14,

2464.—The work is divided into four parts, dealing successively with an historical review of Zr minerals, the salts of Zr, and the metal; exptl. work on Zr; the furnaces used; and a bibliography of Zr and its compds. Analytical methods are given for detg. Zr in ferrozirconium, steel, alloys such as Ni-Zr, and a method of sepn. of Ti, Cr, Ta, and Zr. The phys. and chem. properties of amorphous and coherent Zr are fully listed. The cupferron method is the only one effecting complete sepn. of Zr and Al.

W. H. BOVNTON

Note on alloying tellurium with some white metals. DONALD M. LINNELL. *Chem. Met. Eng.* 25, 268(1921); cf. Ransome and Thieme, *C. A.* 15, 3815.—Al telluride is made by dropping Te into molten Al in a scoria or a porcelain crucible. Al_2Te_3 evolves H_2Te when treated with weak acids or with water. $MgTe_3$ can be made in the same way but care should be taken not to superheat the Mg or the reaction will have explosive violence. *Selenides* can be prepd. in the same way. LOUIS JORDAN

More on the tellurides and selenides. DONALD M. LINDSELL. *Chem. Met. Eng.* 25, 453(1921); cf. preceding abstract.—A Na_2Te soln., if kept from air, is the color of $KMnO_4$. Both Na_2Te and Na_2Se decompose readily from the O of the air, setting free metallic Te and Se with the formation of $NaOH$. This reaction was made the basis for the recovery of these metals by Knorr. LOUIS JORDAN

Preparation of calcium carbide from calcium ammonia and acetylene. L. HACKS-PILL AND E. BOTOLFSEN. *Compt. rend.* 173, 151-3(1921).—Decompr. at 150° of $C_2Ca.C_2H_2.4NH_3$ in an app. entirely of glass (Moissan, *Compt. rend.* 127, 911(1898)) was found not to give pure C_2Ca but a mixt. of this with cyanamide, $Ca(CN)_2$; and free C.

A. R. M.

The action of boric acid on glycerol and on the multivalent alcohols. Application of a new volumetric physico-chemical method. RENE DUBRISAY. *Compt. rend.* 172, 1658-60(1921).—D. applies his new method of analysis (cf. *C. A.* 14, 2433, 2742) by detg. the miscibility of solns. with $PhOH$ to the investigation of the reaction of $B(OH)_3$ on glycerol and mannitol in aq. soln. and in the presence of $NaOH$. $B(OH)_3$ does not form an addition compd. with glycerol in aq. soln., but mannitol forms a compd. which dissociates easily. In the presence of $NaOH$ both glycerol and mannitol form addition compds. which also dissociate easily in aq. soln. E. FIERTZ

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

The joint use of two indicators in the titration of acids and bases. J. L. LIZIUS. *Analyst* 46, 355-6(1921).—One drop of 0.5% phenolphthalein soln. and 3 drops of thymolphthalein soln. (0.04%) may be added to the acid soln. which is to be titrated. The end-point at $p_H = 8.3$ is shown by the red color of the phenolphthalein, but if this point is overstepped a violet color is obtained due to a combination color of the two indicators. Similarly, if the soln. being titrated contains 1 drop of 0.02% methyl red soln. and 3 drops of 0.04% thymol-blue soln., the end-point is shown by an orange color at $p_H = 6$. A drop of 0.1 N alkali in excess causes the soln. to become yellow and another drop produces a blue-green color. It is thus easy to tell whether the proper end-point is reached. W. T. H.

Preparation of alcoholic potassium hydroxide volumetric solution. S. T. McCALLUM. *J. Ind. Eng. Chem.* 13, 943(1921).—By dissolving the KOH in methanol of good quality and filtering off the carbonate residue, a standard soln. of alc. KOH can be prepd. which shows little tendency to darken upon exposure to light. W. T. H.

A method for the determination of the percentage distribution of metals in alloys of which the qualitative composition is known. KARL SCHMIDT. *Chem. Ztg.* 45,

825-6(1921).—*Alloys with two components.* If a_1 represents the at. wt. of metal I, a_2 the at. wt. of metal II, x the % of metal I present, P the wt. of the alloy, V its vol. in cc., s_1 the sp. gr. of metal I and s_2 the sp. gr. of metal II, it can be shown that

$$x = \frac{V(s_2 - P)a_2}{P[(a_1s_2 - a_2s_1)/s_1] - Vs_2(a_2 - a_1)}$$

If the consts. s_1 , a_1 , $(a_1s_2 - a_2s_1)/s_1$ and $s_2(a_2 - a_1)$ be designated by c_1 , c_2 , c_3 and c_4 the equation becomes $x = 100(Vc_1 - P)c_2/c_3 - Vc_4$. *Alloys with three components.* Similarly designating by a_1 , a_2 , and a_3 the respective at. wts. of the 3 components, by s_1 , s_2 , and s_3 the corresponding sp. grs., and by x , y , and q the percentages of each metal present, the following equation can be derived:

$$x = \frac{V[100(a_1 + q(a_2 - a_3)) - P\{100(a_2/s_2) + q[(a_3/s_3) - (a_2/s_2)]\}]}{P[(a_1/s_1) - (a_2/s_2)] - V(a_1 - a_2)}$$

Consts. may also be introduced into this expression as follows: $c_1 = 100/a_1$, $c_2 = a_2 - a_3$, $c_3 = 100(a_2/s_2)$, $c_4 = (a_2/s_2) - (a_3/s_3)$, $c_5 = (a_1/s_1) - (a_2/s_2)$, $c_6 = a_1 - a_2$ and the formula now becomes

$$x = \frac{V(c_1 + qc_2) - P(c_3 + qc_4)}{Pc_6 - Vc_5}$$

With the aid of these formulas the % compn. can be estd. nearly as accurately as by means of quant. analysis. The following consts. have been detd. for use in the above equations.

Alloys of 2 metals.

	a_1	a_2	a_3	a_4
Cu-Ag	+ 10.4900	+ 107.8300	- 33.2048	- 464.8119
Cu-Ni	+ 9.0000	+ 58.6800	+ 5.3883	+ 44.0100
Cu-Zn	+ 6.9200	+ 65.3700	- 16.1086	- 12.4560
Cu-Sn	+ 7.3000	+ 118.7000	- 66.7335	- 402.4490
Sn-Pb	+ 11.6300	+ 207.2000	- 22.4833	- 1005.3600
Sb-Pb	+ 11.3600	+ 207.2000	+ 2.2926	- 988.3200
Sb-Sn	+ 7.3000	+ 118.7000	+ 15.9210	+ 10.9500
Zn-Ni	+ 9.0000	+ 58.6800	+ 26.3388	+ 60.2100
Ag-Au	+ 19.3200	+ 197.2000	+ 1.4884	- 1726.6624
Au-Cu	+ 8.9300	+ 63.5700	+ 27.5788	+ 1193.3159

Alloys of 3 metals.

Ag-Cu-Au	$c_1 = + 6357.0000$	$c_4 = + 3.0883$
	$c_2 = + 133.6300$	$c_5 = + 3.1684$
	$c_3 = + 711.8701$	$c_6 = + 44.3100$

W. T. H.

Methods of gravimetric analysis. XIX. XXIV. Determination of cadmium. L. W. WINKLER. *Z. angew. Chem.* 34, Aufsatzzteil 466-7 (1921); cf. *C. A.* 15, 3427.—Cd can be weighed as $\text{Cd}(\text{NH}_4)_2\text{PO}_4 \cdot \text{H}_2\text{O}$ if the ppt. is formed from barely acid solns. contg. NH_4Cl and dried at 100° . To 100 cc. of soln. contg. 0.15-0.01 g. Cd add methyl orange and make barely acid. Add 2 g. NH_4Cl , heat to boiling and slowly introduce 10 cc. of 20% $(\text{NH}_4)_2\text{HPO}_4$ soln. Heat for an hr. with occasional stirring to make the ppt. cryst. Allow to stand overnight and treat the same as the corresponding Zn ppt. For 0.30 g. of ppt. correct the wt. obtained by adding 0.2 mg., for 0.10 g. add 0.3 mg., for 0.05 g. add 0.4 mg. and for 0.01 g. add 1.0 mg. The ppt. may be ignited and weighed as pyrophosphate and the correction factors are about the same. W. T. H.

The separation of aluminium from beryllium. I. HUBERT T. S. BRITTON. *Analyst* 46, 359-66 (1921).—The 13 best known methods for accomplishing this sepn. are

discussed and expts. are described which were performed to ascertain the best conditions for pptg. $\text{Be}(\text{OH})_2$ by NaOH without pptg. $\text{Al}(\text{OH})_3$. The results of these expts. show that solns. contg. not more than 0.3 g. of BeO and 0.4 g. of Al_2O_3 should be evapd. to about 25 cc., brought to room temp. and carefully treated with 6*N* NaOH until the ptd. hydroxides are just redissolved. Then, after dilg. to 500 cc., the Be may be ptd. by boiling for 40 min.; the $\text{Be}(\text{OH})_2$ ppt. must be filtered immediately. W. T. H.

Estimation of potassium in presence of sodium, magnesium, sulfates and phosphates. H. ATKINSON. *Analyst* 46, 254-5(1921).—Evap. the soln. twice with HClO_4 till fumes are evolved. Cool, add 100 cc. of MeOH and heat with occasional stirring for 1 hr. Allow to stand overnight and filter through a Gooch crucible, washing with 50 cc. MeOH contg. 5% HClO_4 , d. 1.12, and finally with 20 cc. of pure alc. W. T. H.

The determination of vanadium and chromium in ferrovanadium by electrometric titration. G. L. KELLEY, J. A. WILSON, R. T. BOHN AND W. C. WRIGHT. *J. Ind. Eng. Chem.* 13, 939-41(1921).—In H_2SO_4 soln. the Cr and V are oxidized by means of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, any HMnO_4 that is formed is reduced by dil. HCl and the Cr and V are detd. together, by electrometric titration with FeSO_4 soln. In another portion, the V is oxidized to the quinquevalent condition by means of HNO_3 , which does not affect the Cr, and the V is found by reducing to the quadrivalent condition with FeSO_4 soln.

W. T. H.

The determination of metal sulfides by heating in hydrogen sulfide. L. MOSER AND ANNA SCHATTNER. *Chem. Ztg.* 45, 758-9(1921).—Sulfides of Zn, Cd, Mn, Ag and Fe can be ignited in an atmosphere of H_2S and weighed as such and compds. such as the oxides and carbonates of these metals can be converted into sulfides by heating in H_2S . The results of 29 expts. in the detn. of these metals are described; they rarely deviated 0.1% from the truth. The Fe was obtained as FeS . W. T. H.

Complete analysis of impure litharge. W. STAHL. *Chem. Ztg.* 45, 781-2(1921).—Details are given for the detn. of Pb, Ag_2O , Ag, CuO , Bi_2O_3 , CdO , As_2O_3 , Sb_2O_3 , SnO_2 , ZnO , NiO , Fe_2O_3 , Al_2O_3 , MgO , CaO , SiO_2 , SO_3 and CO_2 . For most of the work, a soln. contg. 1-2 g. of ore in HNO_3 is used, the insol. residue being exclud. for SiO_2 , Sn, As, and Sb. The greater part of the Pb is obtained at the start as PbSO_4 from the HNO_3 soln. (cf. *C. A.* 13, 939) and the remainder is recovered from the H_2S ppt. obtained later. As the procedure does not involve any new methods the details cannot be given here.

W. T. H.

The analysis of fluorite. ANON. *Chem. Ztg.* 45, 792-4(1921).—A critical discussion of the various methods which have been proposed for the quant. detn. of fluorine in fluorite. W. T. HALL

The volumetric determination of phosphoric oxide. B. DE C. MARCHAND. *S. African J. Sci.* 17, 259-68(1921).—In a method previously described (*C. A.* 13, 2722) the phosphate was ptd. as NH_4 phosphomolybdate by the Lorenz sulfate-molybdate method, the ppt. dissolved in a measured vol. of standard NaOH and the excess titrated with acid, using phenolphthalein. The ratio of $\text{NaOH}:\text{P}_2\text{O}_5$ was found to be 50:1. This ratio being somewhat different from that used by other chemists it was thought advisable to analyze the ppt. because the ratio formerly detd. was based upon the wt. of ppt. obtained from a known quantity of P_2O_5 . The results of the analysis show that the ppt. as formed by the Lorenz method corresponds to the formula $11\text{NH}_4\cdot 2\text{P}_2\text{O}_5 \cdot 52\text{MoO}_3 \cdot 36\text{H}_2\text{O}$. This formula theoretically calls for 50.5 moles of NaOH for one of P_2O_5 instead of the 50 moles found by expt. The cause for this discrepancy was not detd. Data are given which show the applicability of the method. W. T. H.

The volumetric determination of arsenic acid and arsenates. R. LITCH MORRIS. *Pharm. J.* 106, 480-8, 501(1921).—The processes of A. Williamson, of F. A. Gooch and Browning and of Gooch and Julia C. Morris are discussed in detail. The Brit.

Pharm. process gives varying results with varying conditions of titration. It is vitiated at the start by the fact that the mixing of the reagents alone causes liberation of I₂; on the other hand, upon diln. before titration an error in opposite direction is introduced, i. e., action of the strong acid upon the Na₂S₂O₃ is increased, apparently, by rapid addition of Na₂S₂O₃. To get accurate results by the Brit. Pharm. method, (Gooch and Morris), mix the arsenate soln. with the iodide and the HCl, note the time, then run in the Na₂S₂O₃ slowly, drop by drop, stirring constantly till the yellow color has become faint, and finish the titration five min. after beginning it. Under these conditions, the 2 errors are fairly const. From the amt. of arsenate obtained deduct 0.0040 g. Na₂HSO₄ and calc. %; or, deduct 0.4 cc. from the vol. of Na₂S₂O₃ required. The results should be between 99.8 and 100.2%. Com. arsenate frequently contains nitrate, due to the mode of manuf.; this in contact with HCl in the Brit. Pharm. process will cause extra liberation of I₂.

S. WALDBOTT

The determination of sodium arsenate. C. E. CORFIELD AND ELSIE WOODWARD. *Pharm. J.* 106, 473-5, 501 (1921).—An historical and exptl. survey of the various methods is given. The method of Gooch and Morris (*Am. J. Sci.* 10, 151 (1900)), although somewhat elaborate, is regarded as satisfactory. The inaccuracy, tending towards high results, is small. In order to obtain an accurate result by the method of A. Williamson (*J. Soc. Dyers and Colorists*, May 1896), the calcn. must be made from the 1 reading; or if the Na₂S₂O₃ reading be taken, it must be corrected by means of a blank expt. under exactly similar conditions. In the official Brit. Pharm. method, no allowance is made for the inaccuracy of the Na₂S₂O₃ reading. This would be improved by a subsequent titration with I and a calcn. of result from the value of this titration. As it is, the method gives results about 1% too high.

S. WALDBOTT

Detection and determination of minute quantities of bromide in saline solutions and in a mixture of the halogens. A. J. JONES. *Pharm. J.* 106, 475-7 (1921).—The method is adapted from that of Denigès (*C. A.* 7, 746; 12, 1373). To prep. the reagent (*R*), mix 60 cc. H₂O and 40 cc. H₂SO₄ (Brit. Pharm.). Into the cooled mixt. pour 100 cc. of fuchsin soln. (1 in 1000 of H₂O). After 12 hrs., fill up to 200 cc. Mix equal vols. of this and glacial AcOH; the color is golden yellow. To liberate the Br, J. oxidizes with a mixt. (*M*) of 5 g. KMnO₄, 6.25 cc. H₃PO₄ (d. 1.75), 100 cc. H₂O. Dissolve, boil out traces of Cl, cool, fill up to 100 cc. and pour off from the ppt. To det. Br in a chloride, use a 30 cc. fractionating flask leading to a U tube contg. 5 cc. of *R*; put into the flask (warmed by an oil bath to 85-90°) 5 cc. of a 10% soln. of the chloride, add a drop of dil. thymol blue and just sufficient *N* H₂SO₄ to give not more than a distinct pink color; then add 0.3 cc. of *M*, and H₂O to make 7 cc. Connect the app. and apply suction for 17 min. Soon the Br causes a red or purple color in the U tube. Transfer the color into 7 cc. of CHCl₃ and compare its intensity with standards prep'd. by mixing resp. 0.25, 0.5, 1.0, 1.5, 2, 3 and 4 cc. of 0.001 *N* KBr with 1 cc. of 10% NaCl and 0.3 cc. of *M* and H₂O to make 7 cc. In these concns., the amts. of Cl set free are negligible. NH₄ salts retard liberation of Br; e. g., 0.5 g. NH₄Cl masks 3 cc. of 0.001 *N* KBr. Remove NH₃ by evapg. with NaOH; then neutralize with H₂SO₄ using thymol blue. If in residues to be examd. for Br no NaCl is present, add 0.1 g. triple recrystd. NaCl and proceed as before. The method is sensitive to 1 cc. of 0.001 *N* KBr from 0.3 g. Na₂HPO₄ and 0.1 g. NaCl. From iodides, liberate I with NaNO₂ and dil. H₃PO₄, ext. with CHCl₃ and apply the test to the residual fluid. Certain precautions are detailed. In KI, Brit. Pharm., J. finds 0.0, 0.007, 0.016, 0.04, 0.12, 0.47 and 0.59% KBr; in table salt 0.016% Br, in brine 0.008 or 0.025% Br on saline matter; in BaCl₂ 0.006, and in pure KCl 0.32% Br. S. W.

Determination of nitrates in bismuth salts by means of titanous chloride and Deverda's alloy. THOS. McLACHLAN. *Pharm. J.* 106, 477-8 (1921).—The Brit. Pharm. method for detg. NO₃⁻ is unreliable; the indigo carmine method renders con-

cordant results difficult owing to exact conditions required; the Kjeldahl method is unreliable for Bi subnitrate; and the Ti_2Cl_6 method involves too tedious a process (*C. A.* 9, 1018). The use of Devarda's alloy (*D*) (Cu 50, Zn 5, Al 45) permits a rapid and reliable detn. of the total amt. of Bi subnitrate in any Bi salt except where NH_4 is present. The use of 5 g. of substance is also of great advantage against 0.02 g. used in Brit. Pharm., or 0.2 g. in the indigo carmine method. The proposed method is as follows: Put 5 g. of Bi salt into a distg. flask, add 150 cc. H_2O , 5 cc. EtOH, 50 cc. of 33% KOH, finally 8 g. of *D*, allow to stand for 10 min., then steam distil for 30 min., collect about 100 cc. and titrate the NH_4 . Each cc. of 0.05 *N* acid indicates 0.304% $Bi_2O_3 \cdot H_2O$. Its amt. in 6 samples of Bi carbonate as detd. by the *D* method varied from 0.49 to 3.99%.

S. WALOBOTT

Note on the official method for the determination of hydrocyanic acid. C. E. CORFIELD AND C. J. EASTLAND. *Pharm. J.* 106, 482-3 (1921).—The chief conclusions by R. L. Morris (*C. A.* 14, 2897), that the defect in the Brit. Pharm. process might be due to an insufficient amt. of KI, and that a considerable excess of NH_4 does not interfere with the accuracy of the detn., are reexamnd. by varying the amts. of NH_4 and of KI under otherwise parallel conditions. The results are that an excess of NH_4 (above 20 cc. NH_4OH for each 5 cc. HCN soln. taken) causes a distinct increase in the vol. of 0.1 *N* $AgNO_3$ consumed. Moderate increase of KI has no influence unless amts. above 10 cc. of the official soln. are used.

S. WALOBOTT

The determination of sulfur dioxide in roaster gas. B. C. STUER AND W. GROB. *Chem. Ztg.* 45, 770-1 (1921); cf. 15, 3051.—A polemical discussion regarding the accuracy of the method proposed by A. Sander (*C. A.* 15, 3051) and the priority of the method.

W. T. H.

The determination of sulfur dioxide in roaster gas. A. SANDER. *Chem. Ztg.* 45, 771 (1921).—Values are given for the SO_2 and SO_3 content of the gas from roasters to substantiate the claim that the method proposed by S. (cf. preceding abstract) is sufficiently accurate for ordinary work.

W. T. H.

Determination of sulfur in "Gasmasse." HERMANN C. FLEISCHER. Aschaffenburg. *Zellstoff u. Papier* 1, 73-4 (1921).—The so-called "Gasmasse" (a by-product in the distn. of coal) contains about 45-50% S. This may be detd. by extn. with CS_2 for 1 hr., a Soxhlet or the new extractor of Wislicenus (*C. A.* 15, 3570) being used. Pure S may be obtained by adding 1 g. blood charcoal and 0.5 g. K_2CO_3 to 10 g. of the material and extg. with CS_2 .

C. J. WASSR

A further application of diagrams for waste-gas analysis. K. KUTZNER. *Z. Ver. deut. Ing.* 65, 871-3 (1921).—The proposed diagram of Seufert (*C. A.* 14, 2851) gives a very good idea of the completeness of combustion by merely detg. the CO_2 and O_2 content of the waste gas and it also indicates the excess of O_2 used. On the other hand Seufert's diagram does not indicate with precision the probable CO content of the gas because it does not take into consideration the residual C present in the smoke or left as coke. A mathematical discussion is given, for which the original paper must be consulted, showing how a diagram can be plotted which will take into consideration this residual C and will give a better idea of the utilization of a fuel than does the diagram of Seufert.

W. T. HALL

The estimation of sulfur in oils. HENRY HAUSER. *Anales soc. españ. fis. quím.* 19, 175-91 (1921).—In the method described the substance under examn. is burned in an atm. of O_2 in a 12-l. jar provided with a suitably constructed cover. Substances not readily volatile are absorbed in purified cotton placed in a Pt capsule. Volatile liquids are placed in a tiny lamp made from a small vial. Ignition is effected by means of an electrically heated spiral. After cooling and introduction of a dil. soln. of Na_2O_2 to absorb SO_2 , the vessel is washed out and after the addition of a little Br-water the S is

detc. as sulfate in the combined washings. The method is considered generally applicable to the detn. of S in org. compds.

L. E. GILSON

Method of estimating phenylhydrazine volumetrically and its application to the estimation of pentosans and pentoses. A. R. LING AND D. R. NANJI. *Biochem. J.* 15, 466-9(1921).—This is really an extension of Chalmot and Tollen's method (*Ber.* 24, 694, 3575(1891)) for estg. furfural by pptg. it as the phenylhydrazone; but instead of drying and weighing the latter (a difficult operation) the present authors det. the excess phenylhydrazine volumetrically, according to the equation $C_6H_5NHNH_2 + 2I_2 = 2HI + C_6H_5I + N_2$.

BENJAMIN HARROW

Investigation of zirconium (MARDEN, RICH) 6.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Swedish mineralogical research. G. AMINOFF. *Geol. För. Förh.* 43, 188-201 (1921).—Swedish research in mineralogy has been largely descriptive rather than theoretical partly because the universities have had to emphasize the former viewpoint and partly because Sweden is so rich in mineral deposits. A list (prep'd. by Gust. Flink) is given of 87 unnamed minerals from *Långban* which need to be investigated. All but 3 of these have been found during the past 4-5 years. The descriptions are rather full, occurrence being indicated as abundant, moderate or rare. A monograph on the mines at *Långban* is being prep'd.

W. SÄGERBLÖM

The structure of crystal planes and edges. A. JOHNSEN. Kiel. *Neues Jahrb. Mineral. Geol.* 1918, 49-74.—A general theoretical discussion is followed by an application to the structure of certain faces and edges in *fluorite*. EDW. F. HOLDEN

Certain central sections of the gliding ellipsoids of calcite and rutile. LEONHARD WEBER. Munich. *Centr. Mineral. Geol.* 1919, 353-8.—A discussion of the relations of the crystal axes to the axes of the ellipses cut from the gliding ellipsoid by certain crystal faces.

EDW. F. HOLDEN

Scolecite and metascolecite from Hegeberge, Eulau, Bodenbach. H. MICHEL. Vienna. *Festschrift C. Doelter* 1920, 28-40.—One of the minerals from this locality, which had previously been called okenite, but was recognized to occupy an abnormal place in the paragenetic series, has been further studied. Analysis of a carefully purified sample gave SiO_4 46.44, Al_2O_3 27.08, CaO 13.52, H_2O 13.84, sum 100.88%, agreeing closely with the theory for scolecite. Its physical properties are however different from these of the normal transparent scolecite which is also present, although it agrees optically, having extinction up to 17° and $\alpha=1.509$, $\beta=1.515$. It agrees in its features with the material which had been obtained by Rimme in 1890 by heating scolecite, and was named metascolecite, and is evidently a natural occurrence of this. The mol. changes which are involved in the paramorphism are discussed. It is believed that scolecite was formed at the end of one stage of parogenesis, and then was changed into the metascolecite by an increase in temp. The bearing of the subject on the role of H_2O of crystn. is discussed. Perhaps other alleged occurrences of okenite will prove to be of similar nature.

E. T. W.

Crystallographic study of the datolite from Westfield, Mass. EARL V. SHANNON. *Proc. U. S. Natl. Mus.* 59, 479-539, plates 4(1921).—This paper records the results of an elaborate study of several hundred specimens of datolite, by means of the Goldschmidt 2-circle goniometer and attendant methods. Twenty-four orthographic or clinographic projections are shown and hundreds of measurements are given. Forty-six forms are listed as new to the species.

L. W. RIGGS

Some experimental attempts at forming nickel silicate ores. E. DITTLER. Vienna. *Festschrift C. Doepler* 1920, 15–27.—The various occurrences of Ni-silicate ores are described. New analyses are given of a decompr. product of a characteristic red material, and of an apple-green Mg-Ni silicate which splits apart when wet, both from Frankenstein, Silesia. The latter mineral showed 11.38% NiO. Expts. in extg. serpentine contg. 0.29% Ni with hot H₂O, CO₂ under pressure and Na₂CO₃ solns. yielded no garnierite or pimelite-like silicates, but amorphous material perhaps corresponding to the natural "grauers." Better results were obtained under pressure, and it is concluded that garnierite is being formed in nature by CO₂-bearing surface waters, not by hydrothermal action. The Mg of the serpentine is at the same time turned into carbonates, but pressure seems to be necessary for them to become cryst. E. T. W.

Experiments in the formation of aluminum phosphates. HANS LEITMEIER AND HILDE HELLWIG. Univ. Vienna. *Festschrift C. Doepler* 1920, 41–67.—Considerable uncertainty exists as to the mode of formation of many phosphates. The reported occurrences of Al phosphates where conditions of formation could be more or less definitely detd. are discussed in detail, much chem. data being quoted. Samples of kaolinite, feldspar, and igneous rock, comprising granite and trachyte, were analyzed, and then subjected to the action of (NH₄)₂PO₄ solns. in shaking machines for several months. When the products were analyzed it was found that phosphate minerals similar to those observed in nature had been produced. Higher temps. caused greater P₂O₅ content of the ppts. Pressure would not favor the reactions, however, since the products have greater vols. than the original compds. In some cases evidence was obtained that the feldspars can take up P₂O₅ by a sort of adsorption process or possibly in solid soln. E. T. W.

The identity of flagstaffite and terpinol hydrate. F. M. GUILD. Univ. Ariz. *Am. Mineral.* 6, 133–5(1921).—Further study has shown that the oew mineral flagstaffite (*C. A.* 15, 220) is crystallographically identical with terpinol hydrate. The apparent difference in compn. evidently was due to the material analyzed having been half dehydrated. Both show the same melting phenomena if heated at the same rate. The discovery of flagstaffite thus not only adds a new mineral species, but also brings to light in nature a compd. formerly supposed to be only the product of the synthetic lab. E. T. W.

Kuckersite—study of a marine phylogenetic deposit from the Esthonian Lower Silurian. H. A. R. LINDBERG. *Arch. sci. phys. nat.* 3, 379–413(1921).—Kuckersite is perhaps the oldest deposit of land vegetation and is chemically classed with the sapropels. It differs from boghead coal by its content of O and remains of calcareous organisms. Kuckersite is scarcely attacked by the strong mineral acids or by the usual org. solvents. It rapidly decolorizes Br water thus proving the presence of unsatd. hydrocarbons. Analysis gave ash 3.9%, C 73.68, H 9.29, O + N + S 13.13. Distd. under a pressure of 7 to 20 min. a gas was evolved at temps. from 40° to 60°, at 80° a small amt. of a colorless liquid passed over, at 160° an amber liquid distd. at first, then a blood red tar which formed nearly all of the total distillate. At 202° the distn. was arrested with the evolution of white vapors. The tar was a reddish brown liquid which burned with difficulty, gave a strong green fluorescence, and a characteristic isoprenic odor. The aq. distillate was acid instead of alk. as with coal. Distn. of the tar gave 3.35% acids, 21.42 phenols, 0.23 bases, 0.25 ales., and 74.74 unsatd. hydrocarbons, while satd. hydrocarbons were absent. Many other tests and detns. were made upon kuckersite and its products, and the results compared with the corresponding figures for coal or coal tar. The geology of the deposits is described and a probable genesis of kuckersite proposed. L. W. RIGGS

Mineral statistics. ANON. *Mineral Ind.* 29, 806–87(1920).—Tables of production, imports and exports for all the important countries are given. A. BUTTS

Precious stones. GEORGE F. KUNZ. *Mineral Ind.* 29, 576-606(1920).—The world's production and trade are discussed, covering diamonds, pearls, rubies, jade, etc.

A. BUTTS

Mineral resources of the state of New York. DAVID H. NEWLAND. *N. Y. State Mus. Bull.* Nos. 223, 224, 307 pp.(1919).—"This report is intended to serve the purpose of a general guide to the mineral resources of New York. It presents the principal facts regarding the character, occurrence and production of the useful minerals, with reference to particulars of the local features that bear upon their industrial utilization." For the year 1918 the value of portland cement, brick, pottery, other clay products, gypsum, Fe ore, natural gas, petroleum, salt, sand and gravel other than molding sand, and limestone was over 100 million dollars each; the range being from 1.4 to 7.3 million dollars. The value of garnet, graphite, mineral waters, pyrite, molding sand, marble, sandstone, trap, granite, talc, and Zn ore ranged from \$135000 to \$902000. The total value of the mineral products for 1918 was over 54 million dollars. More than 100 chem. analyses of various mineral samples are recorded. L. W. RIGGS

The manganese-iron and manganite bed of Monte Argentario. LODOVICO EDIMANN. Florence. *Rass. min.* 55, 1-3(1921).—Between Monte Argentario and Orbetello are found deposits of Fe and Mn which are particularly valuable for the electric furnace on account of their very low SiO₂ content. A typical analysis gave: moisture 6.44, combined H₂O 13.01, SiO₂ 0.10, Al₂O₃ 0.09, Fe₂O₃ 1.35, MnO₂ 73.60, Mn₂O₃ 2.33, CaO 1.61 and MgO 1.82%. The Mn ore is found in strata in the calcareous beds, and it is considered to be an amorphous residue deposited from a H₂O soln. circulating in the mineral beds which has evapd. in contact with the air. C. C. DAVIS

Manganese ores of the Island of St. Antico. GINO PARIENTE. *Rass. min.* 55, 4(1921).—In the volcanic materials of which this island is largely composed, Mn deposits are diffused in the tuff. Analysis of the ore extd. from the region between Mercureddu and Poggio Cala Saponne gave Mn 48.06, residue insol. in HCl 6.05%. A sample from poorer tuff gave Mn 38.3; insol. 20.0%. C. C. DAVIS

Monzonite. F. BECKE. Vienna. *Festschrift C. Doeberl* 1920, 5-14.—The history of the rock is described, and the most typical analyses of it are quoted. Norms and Osann consts. are calcd. for these and compared with similar data for other rocks. These are projected in a novel type of *multiple triangular diagram*, and the relations brought out are discussed in detail. It is concluded that the term monzonite can be assigned to a definite rock conception, namely a plutonic rock of granular texture with the essential constituents: magnetite, augite, hornblende, biotite, plagioclase of the av. compn. of andesine, and perthitic orthoclase. There may also be small residual crystns. of either quartz, aegirite, or nephelite, and accessory apatite and titanite. The order of sepn. is that given in the list of minerals, and there is approx. equil. between light and dark minerals and between plagioclase and orthoclase. Chemically $a_2 : c_2 : f_2 = 5.0 : 1.5 : 3.5$, $s = 60$, An:Ab:Or = 20:45:35, Ca:Mg:Fe = 30:30:40. The monzonite magma thus represents a salic end of the differentiation series of either quartz or nephelite-bearing rocks. Analyzed rocks have often been called monzonites when they do not agree with some of the most important of these features, and more care should be used in assigning names. E. T. W.

Mineralogic composition of rockallite. A. LACROIX. *Compt. rend.* 173, 267-73 (1921).—This paper records the results of a petrographic study of the rocks of the island and of the bank of Rockall situated northwest of Ireland in lat. 57.5° N, long. 13.5° W.

L. W. RIGGS

Desilicated granitic pegmatites. SAMUEL G. GORDON. *Proc. Acad. Nat. Sci. Phila.* [1] 73, 160-92(1921).—Previously reported occurrences of albite and phumasiite are reviewed. Occurrences in Pa. are then described, several analyses being quoted.

There is often a regular series of contact zones between albite and serpentine; starting from the center and going out on both sides these comprise: vermiculite, actinolite, talc and serpentine. This series represents a gradual increase in MgO and H_2O in passing outward, and it is concluded that the peridotite was serpentized before the intrusion of the pegmatite magma, and that the mineral zones are due to reaction between magma and wall rock, resulting in desilication. Similar occurrences in N. C. and other states may well be of like origin. A summary of the mineralogy of the desilicated pegmatites is given.

E. T. W.

The relationship between crystallization and slaty cleavage in metamorphic rocks. H. P. CORNELIUS. *Centr. Mineral. Geol.* 1921, 1–11.—The sp. mineral content in metamorphic rocks and their parallel arrangement are essentially independent of each other. Some rocks owe their tendency to cleave entirely to mechanical fracturing (fracture cleavage) unaccompanied by mineralogical changes. Other metamorphic rocks show a more or less complete mineralogical change but no change in structure. In certain regions the same new mineral formation is found in both the massive and schistose phase of the rock. C. concludes that recrystn. is essentially a temp.-pressure phenomenon, accelerated by mechanical granulation. Slaty cleavage is the result of stress. Recrystn. may continue long after the stress has subsided. O. VON S.

Age of the ferriferous beds of the Nurra Mountains in Sardinia. T. SOGNA. Porto Torres. *Rass. min.* 55, 3–4 (1921).—The ferriferous formations of the Nurra Mts. are of Cambrian age. The Paleozoic rocks comprise cryst. schists, clay enclosing beds of oölitic Fe, and volcanic rock. The northern schists differ from the southern in that the latter are micaceous and nodular whereas in the former, ascribed to the pre-Cambriau, similar schists are intercalated with gneiss and magnetite. The gneiss-schists have been proved identical with those of Elba and the fossil beds are analogous to those of Nucie, Bohemia.

C. C. DAVIS

Manganese nodules in Mesozoic deep-sea deposits of Dutch Timor. G. A. F. MOLENGRAAFF AND L. F. DE BEAUFORT. *Proc. Acad. Sci. Amsterdam* 23, 997–1012 (1921).—The distribution and geology of the red deep-sea clay of the East Indian Archipelago are described. Chem. analysis of several samples shows rather close agreement with the av. of 51 samples of recent deep-sea clay analyzed by G. Steiger. The microscopic structure of the clay is described. Mn nodules from the deep-sea clay of Noil Tobee were generally spherical or ellipsoidal in shape and ranged from the size of lemons to that of peas. The nodules have a concentric structure with often a white or gray nucleus free from Mn and consisting of radiolaria which have been largely converted to SiO_2 . H. is <2, sp. gr. = 1.7. Analysis by H. ter Meulen gave: SiO_2 24.4, Al_2O_3 0.8, Fe_2O_3 25.5, MnO 16.9, CaO 1.5, BaO 0.32, MgO 0.34, K_2O 0.15, Na_2O 1.46, NiO 0.28, CoO 0.16, CuO 0.12, O equiv. of Cl – 0.60, H_2O – 7.9, H_2O + 10.2, sum 99.63%. A second type occurs among the Mn nodules of Noil Tobee with H = 6, sp. gr. = 4.2. These closely resemble the Mn nodules near Sua Lain in the island of Rotti in Jurassic marls. Analysis of a Rotti nodule gave: SiO_2 2.9, $(Al_2O_3 + Fe_2O_3)$ 2.3, MnO_2 57.7, MnO 10.5, CaO 5.6, BaO 11.7, Na_2O 1.1, CoO 0.3, H_2O + 15.3, sum 107.4%. [Evidently an error in printing.]

L. W. RIGGS

Rock strata gases in mines of the east Tintic mining district, Utah. G. E. McELROY. *Bur. of Mines, Repts. Invest.* 1921, No. 2275, 3 pp.—Mining operations in 4 of the mines of this district have been hindered by the presence in the rock strata of heavy irrespirable gases which at times flood the lowest working places, also by the abnormally high rock temps. in the lower horizons. These heavy gases range from 60.7 to 75.7% of CO_2 and 39.3 to 23.3% of N. They are satd. with water vapor, are at temps. of 29° to 43° and are 1.25 to 1.40 times as heavy as the adjacent air. These gases have resulted from the oxidation of very finely divided sulfides both in the shale and

in the ore bodies. Oxidation of S produced heat, SO_2 , and H_2SO_4 , thus removing O from the air, while contact of the H_2SO_4 with limestone gave CO_2 . The SO_2 would be constantly reacting with O and H_2O and so disappear, leaving CO_2 and N. Season, weather conditions and especially barometric pressure affect the flow of gas which is greater in winter than in summer. Thorough ventilation with 2 independent sources of power for driving ventilating app. of large capacity should be used. **Hot high-nitrogen gas in a metal mine.** *Ibid* No. 2282.—While studying the heavy strata gases a small local body of light, very hot gas of high N content was observed hanging in a local high spot about $5 \times 5 \times 5$ ft. in size caused by caving at the end of a cross cut. On account of the vapor contained in the gas the bottom level of the gas could be plainly seen and was nearly a horizontal plane of slightly wavy appearance, coinciding with the point where an acetylene light was extinguished. The temp. of this body of gas observed on 3 different occasions was 80° . Air 3 ft. below the vapor line had a temp. of only 49° and a humidity of 27%. At 1 ft. below the temp. was 57° and the humidity 30%. The gas was black damp, defined by Haldane as an accumulation of N and CO_2 in proportions larger than in air and consisting almost wholly of N. Chem. analyses of the gases and adjacent air by G. W. Jones gave the following results:

Sample	Temp.	Humidity.	CO_2 .	O.	N.	Black damp.	Black damp.
						CO_2 .	N.
1	80	100	0.17	8.98	90.90	57.34	0.28 99.72
2	80	100	0.31	7.76	91.93	62.92	0.48 99.53
3	80	100	0.38	2.49	97.13	88.10	0.42 99.58
4	57	30	0.17	20.27	79.56	3.14	4.5 95.5
5	49	27	0.19	20.52	79.29	1.96	8.1 91.9

CH_4 , H and CO were absent. No. 1 was taken 12 in. above the vapor level, No. 2, 18 in. above, and No 3, 4 ft. above and 1 ft. below the roof, No. 4 was taken 1 ft. below the vapor level, and No. 5, 3 ft. below. Sample 3 was taken by water displacement, the others by evacuated bulb. The process of oxidation was still in rapid progress as about 25 cu. ft. of gas per min. was constantly flowing away from a mass of 150 cu. ft. The tendency of the mass of gas to hang to the roof was because of its light wt., being over 90% N. The odor of the gas was musty and sulfurous. In working a stope 50 ft. from the point studied, the heat even with good fan-pipe ventilation was so great as to char the timber sills.

L. W. RIGGS

Carbonic acid and hydrolysis in weathering. E. RAMANN. *Centr. Mineral. Geol.* 1921, 233-41, 266-72.—The process of weathering depends upon the chem. equil. in each case. The agents are chiefly H_2O , CO_2 , and salts (O, restricted to oxidation of ferrous minerals generally). The initial attack of CO_2 and H_2O is not of the same nature but owing to hydrolysis both lead to the formation of OH^- ions; the latter are responsible for silicate decompos.

OTTO VON SCHILCHTER

Magnetic measurements as a method of geologic investigation. FR. SCRIV. *Kali* 15, 231 (1921).—This paper deals briefly with the causes of magnetic anomalies, which are divided into large and local anomalies. The first are related to the oceanic basins, and possibly to gravity anomalies insofar as Fe is the cause of gravity anomalies, but the magnetic anomalies are held to be due to material above a depth of 15 to 20 km., as magnetism disappears at red heat. A reason is given for believing that local anomalies are in many cases related to material much nearer the surface than the figures just mentioned, so that conclusions in regard to tectonic relationships are possible. Five causes of magnetic anomalies are cited: 1. Anomalies related to eruptives or intrusives, which should be considered in connection with gravity anomalies; 2. Fe ores, whatever their source; 3. Folded, dislocated, and overthrust material, which can only be interpreted from any sort of physical measurements with great difficulty; 4. Vertical dis-

placements in nearly horizontal strata. Large scale displacements in fairly horizontal strata may well be followed by magnetic isoanomalous lines when such displacements have once been noted at some point in a given region; 5. Certain "stockförmig" salt deposits show regularities in their magnetic anomalies. Such variations should generally parallel the data for the horizontal component of gravity. In all cases a good deal of geology should be known about a region before magnetic observations are undertaken to assist geology. The magnetic observations are only proposed as applicable in regions not too complicated in place of more expensive methods such as drilling. S. has carefully examined a region in the Mecklenburg salt field and found a correlation between the magnetic anomalies and the general tectonic direction of the deposit, and made a prediction that the salt deposit extends in a particular direction.

R. C. WELLS

A simple device for making crystal-structure models (SPANGENBERG) I. Alsation salts of potash (BEAUVIERIE) 18.

9—METALLURGY AND METALLOGRAPHY

O. J. DEMOREST, ROBERT S. WILLIAMS

Joseph William Richards. ANON. *Chem. Met. Eng.* 25, 730(1921).—Obituary.
E. H.

Aluminium. J. W. RICHARDSON. *Mineral Ind.* 29, 12-9(1920).—A review of the Al industry of the world, with notes on properties and metallurgy. A. BUTTS

Antimony. K. C. LI. *Mineral Ind.* 29, 24-34(1920).—The Sb market is directly affected by the price of silver. The use of Sb oxide, especially for the white pigment, gives considerable promise. Statistics of production, prices, and trade are given. A. BUTTS

Antimony in 1920. FRANK C. SCHRADER. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part I, 73-84 (preprint No. 8, published Oct. 27, 1921). E. H.

Bismuth. A. T. WARD. *Mineral Ind.* 29, 64-6(1920).—Sources of Bi, world's production, and uses are given. A. BUTTS

Cadmium. A. T. WARD. *Mineral Ind.* 29, 72-3(1920).—Notes on sources, uses, and output. A. BUTTS

Chromium. SAMUEL H. DOLBEAR. *Mineral Ind.* 29, 88-92(1920).—Production and trade in chromite and Cr compds. are reviewed, with a bibliography. A. BUTTS

Cobalt. C. W. DRURY. *Mineral Ind.* 29, 139-41(1920).—Output, trade, and uses are discussed. A. BUTTS

Copper. WALTER HARVEY WEED. *Mineral Ind.* 29, 142-174(1920).—A review of the world's Cu industry, covering production, mining conditions, prices, U. S. imports and exports, etc. A. BUTTS

Metallurgy of copper in 1920. L. S. AUSTIN. *Mineral Ind.* 29, 175-225(1920).—A review of articles and new developments. A. BUTTS

Gold and silver. M. W. VON BERNEWITZ. *Mineral Ind.* 29, 241-325(1920).—A review of the industry, including markets, world production and mining conditions, and metallurgical progress. A. BUTTS

Gold, silver, copper and lead in South Dakota and Wyoming in 1919. CHARLES W. HENDERSON. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part I, 615-20 (preprint No. 22, published Oct. 5, 1921). E. H.

Iron and steel. EDWIN F. CONE. *Mineral Ind.* 29, 349-404(1920).—Statistical review of the world's iron and steel industry, with notes on technology and data on electric furnaces. A. BUTTS

Iron ore, pig iron and steel in 1919. ERNEST F. BURCHARD. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part I, 621-52(preprint No. 23, published Oct. 14, 1921). E. H.

Lead in 1919. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part I, 313-30(preprint No. 15, published Oct. 6, 1921). E. H.

Lead in 1920. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part I, 85-95(preprint No. 9, published Oct. 14, 1921). E. H.

Lead. H. B. PULSIFER. *Mineral Ind.* 29, 405-24(1920).—Discussion and statistics of the industry in the U. S. and other countries are given. A. BUTTS

Metallurgy of lead in 1920. J. LABARTHÉ. *Mineral Ind.* 29, 425-36(1920).—A review. A. BUTTS

Manganese. MARSHALL HANEY. *Mineral Ind.* 29, 443-9(1920).—Production, imports and prices are covered. A. BUTTS

Molybdenum. W. NORMAN BRATTON. *Mineral Ind.* 29, 458-89(1920).—The Mo market, metallurgy, and world's resources and production are discussed. A. BUTTS

Nickel. THOMAS W. GIBSON. *Mineral Ind.* 29, 478-88(1920).—A discussion of deposits, metallurgy, and production, with statistics. A. BUTTS

Platinum. GEORGE F. KUNZ. *Mineral Ind.* 29, 546-64(1920).—Production, trade, prices and sources are covered. A. BUTTS

Quicksilver. W. D. BURCHAM. *Mineral Ind.* 29, 607-14(1920).—The market and production in the U. S. and other countries are treated. The U. S. 1920 output was the lowest on record. A. BUTTS

Tin. BALIOL SCOTT. *Mineral Ind.* 29, 659-78(1920).—A discussion of the world's output, mining conditions and market. A. BUTTS

Titanium and zirconium. ANON. *Mineral Ind.* 29, 677-80(1920).—Sources, production and uses are reviewed. A. BUTTS

Tungsten. COLIN G. FINK. *Mineral Ind.* 29, 681-704(1920).—Market, imports, world's production, and technology are covered, with bibliography. A. BUTTS

Uranium and vanadium. R. B. MOORE. *Mineral Ind.* 29, 705-12(1920).—A discussion of ore deposits, production, metallurgy, uses, etc. A. BUTTS

Zinc in 1919. C. E. SIEBENTHAL AND A. STOLL. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, part I, 653-64(preprint No. 24, published Oct. 13, 1921). E. H.

Zinc. JESSIE A. ZOOK. *Mineral Ind.* 29, 713-39(1920).—A review of the world's industry. A. BUTTS

Metallurgy of zinc in 1920. W. R. INGALLS. *Mineral Ind.* 29, 739-47(1920).—A discussion of present conditions and technical improvements in the Zn industry. A. BUTTS

Progress in ore dressing and coal washing in 1920. ROBERT H. RICHARDS AND CHARLES E. LOCKE. *Mineral Ind.* 29, 748-805(1920).—Crushing and grinding, screening, classifying, settling, jigs, tables, magnetic concn., flotation, and accessory app. are treated, with flow-sheets and examples from practice and a complete bibliography for the year. A. BUTTS

Preliminary roughing concentration by sorting, jiggling and tabling. EDWARD S. WIARD. *Eng. Mining J.* 112, 326-30, 369-73, 411-7(1921).—A discussion of principles, with illustrative data and expts. A. BUTTS

Distribution of gold in basket ore classified products with reference to milling and cyaniding operations. F. WARTENWEILER. *J. Chem. Met. Soc. S. Africa* 31, 217-22 (1921).—By means of oil flotation samples of slime charge, slime residue, and cyanide pulp were sepd. into pyritic and gang portions and the distribution of Au was detd. Results are shown in tables. The argillaceous and siliceous portion of the slime residue contains 60% of the Au, while the Au in the cyanide pulp is found to the extent of

87.5% in the pyrite portion. The Au in the pyrite portion of the slime charge dissolves readily in cyanide soln. Encased free Au is reached and dissolved by the cyanide. The amt. of Au amalgamable in cyanide pulp and sand charge (37.5% and 19.4%, resp.) varies with the fineness of grinding. The tendency in practise to throw more responsibility for Au recovery on the cyanide and less on amalgamation is confirmed. It is of great importance to grind the max. amt. of pyrite and Au to pass at least 200-mesh in order to obtain the highest extrn. The importance of careful classification and tube-milling follows.

LOUIS JORDAN

Improvements in nodulizing at Chrome, N. J. C. L. COLBERT. *Eng. Mining J.* 112, 255-7(1921).—The satisfactory nodulizing of flue dust on fine ores at the U. S. Metals Ref. Co. at Chrome, N. J. is accomplished by a mechanical agglomerator which consists essentially of a set of rolls through which the plastic material from the rotary kilns is passed and compressed together. The kilns are fired by a stationary powdered coal combustion chamber at the discharge end. This method of nodulizing conserves S which has always been low in the ores received at Chrome. R. S. DEAN

Calculation of equilibrium in metallurgical reactions. PAUL D. MGRICA. *Chem. Met. Eng.* 25, 608-12(1921).—Thermochem. computations are applied to furnace reactions. Thermal data make possible reliable inferences as to stability, oxidizability, reducibility, equil. conditions, etc. Predictions based on heat of reaction are only reliable when pure solids or liquids not solutions are involved, (condensed systems). They are not applicable to gas reactions at high temp. Simple thermodynamic laws modified by a few assumptions are used for calcs. which enable one to predict with certainty whether a reaction should proceed. J. O. HANDY

Production of pig iron containing manganese from low manganese residues, especially Siegerland blast-furnace slag. H. THALER. *Stahl u. Eisen* 41, 249-53, 338-43 (1921).—Siegerland blast-furnace slag contg. 12.2% MnO was mixed in varying proportions with Fe ore and reduced by C in an elec. furnace with Ca phosphate and lime-stone as a flux. Pig Fe contg. Mn and Fe-Mn alloys were obtained. The cost seems to be such as to make the process commercially feasible. R. S. DEAN

New Trumbull-Cliffs 600-ton blast furnace. ANON. *Iron Age* 108, 673-8(1921).—A detailed description of the arrangement and equipment of a new 600-ton blast-furnace plant at Warren, Ohio, for the Trumbull-Cliffs Furnace Co. LOUIS JORDAN

Strength of blast-furnace slags. H. BURCHARTZ. *Stahl u. Eisen* 41, 472-5(1921).—Expts. on 10 samples of blast-furnace slag showed that the dark color due to Fe and Mn was in general associated with high mechanical strength and resistance to wear. R. S. DEAN

Spectroscopic examination of converter flame. W. J. CAMPBELL. *Chem. Met. Eng.* 25, 618(1921).—By the use of the spectroscope continental European makers of Bessemer steel castings are able to make good castings of 0.40 to 0.60% C without taking the blow completely down and then recharburizing as is done in Great Britain. The metal being hotter there is less waste from short-run castings. Observation of the flame by eye alone does not give definite information as to the stage of C elimination. The intensity of the green C lines in the blue and green parts of the spectrum is the indication which the observer learns to coördinate with definite percentages of C in the remaining metal. The practice is general in Belgium and in Sweden. It should be adopted in England. JAS. O. HANDY

Discussion on open-hearth practice. HENRY WM. SELDON. *Blast Furnace & Steel Plant* 9, 460-70(1921).—Efficiency of fuel-gas consumption is an important consideration. The use of too little air to burn the gas is a common condition. A. BUTTS

Discussion on open-hearth practice. HENRY WM. SELDON. *Blast Furnace & Steel Plant* 9, 521(1921).—In the manuf. of medium-C steel there is often considerable

variation between the compn. of a ladle-test and of the ingots poured from the bottom of the ladle, the C, P, and S having segregated to some extent to the bottom. This condition was aggravated in heats where large additions of ferro-Si had been made in the ladle, and it appeared that the cause was the fact that the slag had become too acidic. Adding CaO to the ladle eliminated the segregation. Analyses are given. A. BURNS.

Steel foundry makes sugar-mill machinery. JAMES J. ZIMMERMAN. *Blast Furnace & Steel Plant* 9, 536-40(1921).—A discussion of the properties and manuf. of the materials used in making roll shells and shafts. For the roll shells charcoal iron made in an air furnace is much superior to cupola iron, chiefly on account of the refining action and better control in the air furnace. For roll crushers steel is better than either. For shafts wrought iron and steel are used. Steel has greater tensile strength, but wrought iron is preferred on account of its fibrous structure, which makes it not liable to sudden failure.

A. BURNS

Use of the scleroscope on light specimens of metals. FRED S. TRITTON. *J. Inst. Metals* (advance copy), No. 8, 10 pp.(1921); *Engineering* 112, 492-3(1921).—The expts. were undertaken with the view of finding out whether errors exist when the ordinary methods of support are used and, if so, to find some method of support that will eliminate them. The results show that the usual methods of supporting light specimens of metal for the scleroscope test do not give results with the accuracy that can be obtained when the specimens are mounted in a layer of pitch less than 0.025 in. thick and held by means of a clamp. Another method that gave excellent results was devised in which the bottom of the specimen, which must be perfectly flat, is smeared with glucose and pressed or wrung with a sliding action on to a flat-topped steel base, weighing at least 1 lb. The whole surface of the specimen is then perfectly supported for testing purposes. It is necessary to see that no air bubbles are trapped in the glucose beneath the specimen. The specimens may be mounted on a sep. base in order to avoid getting glucose on the hammer or the surface under test. The results of tests on specimens, when attached with glucose to supports of various metals, are shown in a table and indicate that the rebound of the hammer is slightly affected by using the different metals even when the specimen is $\frac{1}{4}$ in. thick.

V. O. HOMERBERG

Graphical representation of systems of more than three components and a method of logarithmic representation. R. KRULLA. *Z. Metallkunde* 12, 81-4(1920). R. S. W.

Electrolytic etching of metals. FRANK ADCOCK. *J. Inst. Metals* (advance copy), No. 11, 9 pp.(1921).—Cathodes of Pt gauze were used in all cases, and suitable resistances were employed to regulate the strength of the continuous current through a range of $\frac{1}{1000}$ to about $1\frac{1}{2}$ amps. A discussion is given on the effects of a number of etching solns. on various metals and alloys. A number of photomicrographs are included.

V. O. HOMERBERG

Changes in the tensile properties of metals with alternating stresses. P. LUDWIK. *Z. Metallkunde* 11, 157-68(1919).—A discussion of the connection between alternating stresses and tensile properties from the mechanical engineering standpoint. Many curves showing mechanical properties are given.

R. S. W.

Extrusion defect. R. GÄNDERS. *J. Inst. Metals* (advance copy) No. 7, 9 pp.(1921).—When solid rod is extruded from a central die, the last 25 or 30% of rod to leave the die contains a characteristic defect peculiar to extruded rod. Transverse sections show a more or less complete circle, varying in diam. at different positions along the rod, consisting of oxide and foreign matter enclosed in partially deincised bases. The core inside the circle has generally the same structure as the sound metal outside. Typical examples are shown by photographs. The mode of formation of the defect was investigated by the examm. of billets extruded to various stages. The specimens were sectioned axially and pickled in 50% HNO₃. In such specimens the foreign matter

and deoxidized metal similar to that dividing the core from the outer ring in the bar is present in the partially extruded billet in the form of a funnel. The mouth of the funnel is the edge of the rear end of the billet, and the neck of the funnel is continuous with the tubular defect in the extruded rod, while the metal within the funnel is sound. An explanation given for this defect involves the chilling of the outer surface of the heated billet when it comes in contact with the relatively cool receiver and thereby becomes less plastic than the interior. The actual defect appears to consist of the dirty, oxidized skin of the original billet. Several methods are suggested for the prevention of the entry of the skin of the billet into the metal. Possible methods are: (a) to avoid chilling the surface of the billet when extrusion begins, (b) to trap the skin at the rear end or to provide an outlet, (c) to extrude through an eccentric die, (d) to avoid relative movement of the receiver and billet. This last method proved the most successful. Details as to the app. used and the method of extrusion are given. In complete extrusions the rod produced was sound from end to end.

V. O. HOMERBERG

The formation of twins by cold-work in the surface layers of metals. RUDOLF VOGEL. *Z. anorg. allgem. Chem.* 117, 271-80 (1921).—The lines appearing as cross-hatching on twin crystals in polished and etched sections of cold-worked ductile metals and alloys are the result of cold-work on a thin surface layer of the metal. Polishing causes sufficient cold-work to produce them. They disappear if the specimen is heated under the proper conditions to produce recrystn. of the metal. These lines are similar to the Neuman lines seen on the etched surfaces of meteorites. It is very probable that the Neuman lines correspond to twinned lamellae.

F. P. FLAGG

"Characteristic curves" of the heat treatment of steels. ALBERT M. PORTEVIN AND PIERRE CHEVRENIARD. *J. Iron Steel Inst.* 1921, (advance copy), 19 pp.—The representation of the result of a treatment is made graphically by plotting the 2 fundamental factors of heat treatment, the temp. of heating and the rate of cooling, as coordinates. This method leads to the establishment of what the authors term the "characteristic curves" of the heat treatment of the steel in question. Such curves not only combine, within a single diagram, the fundamental data of every possible heat treatment, but they also afford a means of defining accurately the annealed and hardened states of the particular steel, and, therefore, constitute the basis and indispensable preliminary of every treatment properly carried out with a particular object. In order that such a graphic representation may be plotted properly, it is necessary that the values from which it is built up shall be susceptible of numerical definition so as to be capable of measurement. The authors describe how they evaluate the rate of cooling and how they define the final state, that is to say, the result of the treatment. V. O. HOMERBERG

Constituents found in tungsten and molybdenum steels. ALBERT M. PORTEVIN. *J. Iron Steel Inst.* (advance copy) 1921, 4 pp; *Engineering* 112, 372-3 (1921).—P. has studied the structural variations resulting from annealing, and then cooling very slowly, steels contg. 0.1-0.4% W. The structure of these "normal" steels is described as consisting of ferrite associated with pearlite, or as being devoid of pearlite. After annealing at about 1300°, followed by a cooling extending over 75 hrs., down to 200°, the structure is completely altered. A steel contg. 0.4% C and 5.4% W showed microscopically a network formed of light and dark areas sepg. regions occupied by a constituent different from any hitherto known. This is apparently a complex, consisting of needles colored by a soln. of Na picrate, and proved to be a tungstate Fe_3W . In W steels a structure comprising 4 constituents is encountered; a tungstic ferrite, a W carbide, a tungstic troostite, and a new constituent which is a complex ferrite + Fe_3W . P. found in Mo steels, annealed as previously described, a constituent presenting the same morphological characteristics and susceptibility to etching as the acicular complex in W steels. Instead, however, of occurring as it does in the steel contg. 0.4% C and 5% W,

in masses regularly distributed and forming the interstitial packing between a network of C complex, this constituent is found in irregularly disseminated clusters in a ground mass very readily colorable by acid reagents and hence more highly carburized.

V. O. HOMERBERG

Slip interference theory of hardening. HAAKON STYR. *Chem. Met. Eng.* 25, 313-14(1921).—S. believes that diffusion at high temps. and in the molten state is readily explained by assuming the solute to be distributed in the mol. state, and that cementite dissolves in this manner when taken up by Fe. This is denied by Jeffries and Archer (*C. A.* 15, 2824). The results of various writers are set forth in order that it might be reasonably concluded that in hardened steel, cementite is in soln. in the traces of γ -Fe left after most of the α -Fe has formed. The Fe_3C mols. are still in soln., perhaps polymerized, and, with the γ -Fe, forming a kind of gel in the Fe, but not separated as crystals of cementite. In such form the dissolved cementite mols. may well be considered as keys on the slippage planes of Fe. V. O. HOMERBERG

Slip interference theory of hardening. ALBERT SAUVEUR. *Chem. Met. Eng.* 25, 509-12(1921).—S. is prepared to accept the idea set forth by Jeffries and Archer (*C. A.* 15, 2824) that martensite contains α -Fe, but desires more evidence on the contentions that its hardness is due to sub-microscopic grain size, that an intermetallic compd. cannot exist in a state of solid soln., and that the carbide Fe_3C , therefore, cannot be present in solid soln. in γ - or α -Fe. V. O. HOMERBERG

Slip interference theory. NICKOLAS T. BELAIEV. *Chem. Met. Eng.*, 25, 584(1921).—Some of the facts derived from the study of damascene steel tend to support the general views of Jeffries and Archer (*C. A.* 15, 2824). B. agrees with J. and A. that martensite is α -Fe but considers martensite as a pseudo soln., not of C, but of cementite in α -Fe; and further that not only the fineness of grain but chiefly the "Widmanstätten" structure of the deformed elemental octahedron is responsible for the hardness. V. O. H.

Slip interference theory of the hardening of metals. ARNE WESTGREN. *Chem. Met. Eng.* 25, 641(1921).—By means of X-ray spectrographic investigations of metals W. came to the same conclusions regarding the hardness of solid solns. as Jeffries and Archer (*C. A.* 15, 2824). W. does not agree with J. and A. that C in martensite is dispersed in the form of atoms but believes that martensite really contains cementite in the form of Fe_3C mols., and even as very small Fe_3C cryst. grains. W. takes exception to the reason given by J. and A. for the assumption that C is dispersed in the form of atoms in martensite. The reason given for this assumption is that it is impossible for C atoms to migrate freely in the metal if they are in contact with particular Fe atoms. W. states that each C atom can very well be connected with 3 Fe atoms and yet easily travel in the metal, since during the displacement it merely changes its companions. V. O. HOMERBERG

Damascene steel. N. T. BELAIEV. *J. Iron Steel Inst.* 1921, (advance copy), 4 pp., *Engineering* 112, 395(1921).—In damascene steel the degree of spheroidization is always very high. That spheroidization, however, was not an end in itself for the ancient maker, but was attained incidentally during the numerous cautious forgings and heatings, when the greatest ductility was sought and obtained. In high-speed steels that spheroidization is also attained, but it seems to B. that insufficient stress has been laid on that point, either by the maker or the user of high-speed steel. A scientific application of the spheroidizing process would help to improve the qualities of high-speed steel. Another inference from the damascene process might be drawn, namely, the proper study of the macrostructure. V. O. HOMERBERG

Constitution of martensite and troostite. D. J. MCADAM, JR. *Chem. Met. Eng.* 25, 613-8(1921).—The conclusions of Jeffries and Archer (*C. A.* 15, 2824) in regard to the

causes of the hardness of martensite seem to be confirmed by expts. at the U. S. Naval Engineering Expt. Sta. on the effect of temp. on the grain coalescence tendency of ingot Fe. If the term "martensite" is to be limited so as to apply only to the constituent of steels in which the allotropic expansion but not the carbide contraction has occurred, the constituents, usually designated "martensite", of some hyper-eutectoid steels should be known as "hyper-eutectoid troostite." Martensite consists of α -Fe with "austenitic carbide" in suspension. In troostite, the austenitic carbide has undergone the "carbide contraction" to form cementite particles of the smallest size that can exist independently.

V. O. HOMERBERG

Does the critical point depend on the strength of the magnetizing field? KOTARO HONDA. *J. Iron Steel Inst.* (advance copy) 1921, 6 pp.—The specimens used contained 0.0085, 0.68 and 1.17% C. The magnetizing field varied from 400 to 2150 C. G. S. units. A torsion-balance was used for the accurate detn. of the critical point in the different magnetizing fields. The measurement of the magnetization at high temps. was made in a vacuum in order to avoid oxidation of the specimens. It was found that the critical point is not affected by the magnetizing field. The magnetic or A_2 transformation is very probably a progressive change going on in the mols. themselves with the rise in temp., and the change of magnetization is only one aspect of this transformation as revealed magnetically.

V. O. HOMERBERG

Some properties of molybdenum steels. ANON. *Engineering* 112, 350-1 (1921).—The action of Mo in fractional percentages intensifies the excellent qualities of other alloy steels supplying in these steels certain qualities without which they are limited in their application. In special steels in which Cr, Ni and V play an important part, the heat treatment is effective within rather narrow limits of temp. Outside of this small range, their high-grade qualities are seriously impaired. For these steels Mo acts as corrective and greatly extends the range within which heat treatment is beneficial. By its use, segregation is prevented, uniformity of texture is promoted and toughness is imparted. Mo increases considerably the tensile strength of C and Ni steels. In Cr-Ni steels, probably owing to the formation of double carbides, additional tensile strength, hardness and other beneficial qualities are imparted. The penetrative effect of heat treatment in large sections is decidedly improved. Mo steels can be subjected to wide temp. changes for both hot working and heat treatment. Mo steel can be machined more easily than other steels of equal physical properties. V. O. HOMERBERG

Three types of alloy sheet steel. III. HORACE C. KNERR. *Iron Age* 108, 725-8 (1921); cf. *C. A.* 15, 3807.—Elec. and acetylene welding details and their effect on the physical properties are given. Tests were made with chrome-V, Ni-Cr, and 3.5% Ni steel. Chrome-V steel was adopted as the most satisfactory. V. O. HOMERBERG

The magnetic properties of electrolytic iron. E. GUMILICH. *Stahl u. Eisen* 41, 1249-54 (1921).—Several samples of electrolytic Fe were examd. for their magnetic properties both before and after heat treatment. The samples were from the Langbein-Pfauhauser works in Leipzig, from the Griesheim-Electron chem. works in Bitterfeld and from Dr. Franz Fischer. Repeated annealing or melting *in vacuo* greatly improved the magnetic properties of all the irons. The lowest coercive force was obtained with Fischer's Fe, which on annealing at 1000° gave the previously unreachd value of 0.11. B for $H=150$ was about 18000 for all the irons. While the initial permeability varied from 98 for the Pfauhauser Fe melted *in vacuo* and forged to 400 for doubly refined Fe from Griesheim annealed at 950°. The general conclusions are that electrolytic Fe is not the best or most economical for instruments or machines requiring high magnetizing forces but that for work requiring low magnetizing forces as in telephony the untreated electrolytic iron is well suited since it combines high initial permeability with high elec. resistance and hence low eddy current losses.

R. S. DEAN

Case hardening and oxidation of steel. FEDERICO GIOLITI. *Chem. Met. Eng.* 25, 312-13(1921).—Matsubara (*C. A.* 15, 1683) does not sufficiently explain his manner of deducing equil. data in a vessel, of which only a part is heated to the reaction temp. to be studied and the rest (about $\frac{1}{4}$ of its length) is cooled by circulating H_2O . Also, no reference is given to the time required to withdraw the gas contained in the reaction chamber, which gas cannot be in a true physical and chem. equil. These points and many others in the paper require a complete discussion if the exptl. results are to be taken as a sure basis of a new theory in open opposition to the results of previous investigators.

V. O. HOMBERG

Microscopic examination of iron and steel. ANON. *Chem. Met. Eng.* 25, 471-2 (1921).—Tentative methods for testing Fe and steel, as proposed by a committee on metallurgy, appointed by the Am. Soc. Test. Materials, are given. The location of test pieces, method of polishing, methods of etching with the formulas and actions of various reagents are considered.

V. O. HOMBERG

A metallographic characteristic for determining the temperature of previous annealing of low-carbon steel. P. OSERHOFFER. *Stahl u. Eisen* 41, 1215-7(1921).—In steel with 0.07-0.12% C annealing between A_{c1} and A_{c2} produces a characteristic structure. This structure is essentially the sepn. of the pearlite in halos around the ferrite grains, and is due to the soln. of the pearlite in the ferrite above A_{c1} and since it does not diffuse rapidly much of the ferrite remains unchanged. Hence on cooling, the pearlite seps. as halos at the old crystal boundaries.

R. S. DEAN

Influence of the width of the specimen on the results of tensile tests of mild steel and rolled copper. T. HUDSON BEARE AND WM. GORDON. *Engineering* 112, 389-91(1921).—The main object of the expts. was to det. the nature of the influence of the width of the specimen upon the apparent strength and ductility of the metal under test. Metal of const. thickness was employed in each expt. The thickness of the steel specimens was $\frac{1}{4}$ in. with 0.12 to 0.15% C in the first series. In a second series the thickness was $\frac{1}{8}$ in. with 0.13% C. The strips of Cu were $\frac{1}{16}$ in. thick. A table is given to show the effect of variation of width of specimen on the yield point, tenacity and mean breaking stress. The width of the test bar appears to have no appreciable influence upon the elastic strength of mild steel or rolled Cu. The tenacity also appears to be but little affected. The extension and the reduction of area are considered. The reduction of area for the $\frac{1}{4}$ -in. steel bars drops rapidly in value as the ratio of width to thickness is increased from 2 to 6, then remains practically const. up to the value of 16 for the ratio. Similarly, the reduction for the $\frac{1}{8}$ -in. steel bars drops rapidly between the ratios 2 and 6, then falls gently but steadily towards the ratio 32. The best curve for the Cu bars is a straight line, which has no initial drop.

V. O. HOMBERG

Factors affecting the life of machine-gun barrels. W. W. SVYSENIKOFF. Bur. Standards, *Tech. Papers* No. 191, 27 pp.(1921).—The investigation indicates that when a machine-gun barrel reaches its life limit its exhaustion is due to a combination of the abrasive action of the bullet and abrasion by hot gases, but to a greater degree to the former. Expts. with the elec. arc show that the rapid cooling (which is due to the large mass of cold metal near the highly heated inner surface of the steel) from temps. near the m. p. of the metal produces a martensitic layer. A similar layer is produced in the firing of a machine gun, indicating that the temp. conditions for the development of martensite can be made by the elec. arc to approach those which occur in the gun under actual fire. The selective hardening of the steel sets up surface strains, and the surface of the bore is readily cracked on account of the dimensional changes of the hardened brittle surface of the steel resulting from sudden changes in temp. between separate shots. The cracks that originate at irregularities in the surface of the bore are attributable to the method of manuf. of the barrels.

V. O. HOMBERG

The 1921 fall exhibition at Leipzig. F. MOSER. *Chem. App.* 8, 153-6(1921).—A new acid-resisting Fe-Si alloy, "Thermasilid," was exhibited by the F. Krupp Co. Comparative 9-hr. tests of acid-proof cast Fe and "thermisilid" in 1:10 acids at 100° gave the following comparative losses in g.: H₂SO₄, 318:5; HCl, 358:3; in an 18-hr. expt. with dil. H₂SO₄ the respective losses were 210:2. J. H. MOORE

Aluminum-copper alloys. R. J. ANDERSON. *Trans. Am. Electrochem. Soc.* 40, preprint (1921); cf. *C. A.* 15, 359.—A review. C. H. ELDRIDGE

Casting aluminium-zinc alloys. F. A. LIVERMORE. *Chem. Met. Eng.* 25, 516 (1921).—In melting Al alloys, plumbago or salamander crucibles (preferably with clay liners) should be used. Melting is best carried out in a gas-fired furnace using a mixt. of air and gas, which can be adjusted to prevent overheating and subsequent burning of the metal. No charcoal or carbonaceous covering should be used. The pouring temp. has a very noticeable effect upon the resultant castings. In general, the temp. should be as near to the m. p. as possible. The temp. recommended is 650° ± 10°. V. O. HOMBERG

The magnesium alloy "electron." S. BECKINSALE, *J. Inst. Metals* 1921 (advance copy), 2 pp.—The samples examd. contained about 95 Mg, 4.5 Zn and 0.5% Cu. They were in the form of rod, probably extruded at a raised temp. One sample showed evidence of having been subjected to cold heading. The alloys machined well, and compared very favorably with Al alloys in tensile properties (allowance being made for the much lower sp. gr.), but they were not so ductile in compression. Also in *Engineering* 112, 641(1921). V. O. H.

Decomposition of a cap screw of copper-aluminium-zinc alloy. O. BAUER. *Z. Metallkunde* 12, 129-31(1920).—The cap screw was an alloy with about 5% Cu, 2% Al, 1% Pb, small amts. of Fe and Sn with the balance Zn. Ixamm. with a low-powered microscope showed a bright, cryst. outer zone and a dull gray inner zone. Magnification of 200x showed a definite transition from the sound to the badly decompd. material. The cap was taken from a boiler and B. believes that the decompn. was due to liquid water and contact of the screw with a "nobler" metal than Zn. B. concludes that Zn-rich alloys must never be used in connection with steam boilers if there is any chance of contact of the alloy with condensed steam. Drawings and photomicrographs are given. R. S. WILLIAMS

A discussion of thermo-electricity in alloys forming solid solutions. C. BORELIUS. *Z. Metallkunde* 11, 169-79(1919).—Coud. measurements have shown characteristic curves for various alloy types and it was thought that thermo-elec. relations might be similar. This was found not to be true and in an attempt to discover such relationships as exist B. has compiled published data on thermo-elec. effects, the Peltier and the Thomson heat effects. The curves plotted from these data indicate a marked similarity in the curves of metals in the same natural group of elements but no general similarity in solid solns. B. believes that breaks in these curves suggest definite at. configuration in certain solid solns., indicating the existence of compds. in soln. The most probable compds. are AuPd, AgPd, and CuNi (constantan). R. S. WILLIAMS

New experiences with light metal alloys in high speed motors. VON SELVE. *Z. Metallkunde* 13, 316-8(1921).—S. discusses the successful use of Al alloys in many motor and airplane parts. Expts. were made with Mg alloys because of their lighter wt. While they were found practicable from an engineering standpoint, they are less resistant to heat than the Al alloys and their durability has not yet been detd. In addition to cast alloy pistons, S. has made pistons by a drawing operation similar to that used in making cartridge cases, producing pistons lighter in wt., stronger and more durable than the cast alloys. R. S. W.

Casting of brass ingots. R. GENDERS. *J. Inst. Metals* 1921 (advance copy) No. 3,

4 pp.; *Engineering* 112, 452(1921).—In expts. that were carried out to minimize the occurrence of non-metallic inclusions, the first step taken was to adopt a form of ingot the length of which was not great in proportion to the cross-sectional area. The ingots made were 3 in. square and 30 in. in length. Steel-making practice was followed in introducing a hot sinking head or "dazzle." The nozzle (a short fireclay sleeve) is heated to the melting furnace temp. and inserted in the top of the mold, resting on a small ledge. A sketch is given of the arrangement. The molten brass is poured through the nozzle, which is filled to the top. No pipe is formed in the ingot proper, the metal in the nozzle remaining quite fluid and sinking gradually, with level surface, to feed the contraction of the ingot below. Additions of metal may be made at any time to the metal in the nozzle without risk of introducing defects into the ingot, any dross rising to the top of the still fluid head. The nozzle is an automatic feeder and there is no need to discard any of the top end of the ingot beyond the metal that has finally solidified in the nozzle. Central shrinkage cavities were avoided by regulating the rate of pouring so that the ingot, when just completely poured, had a fair temp. gradient from bottom to top. This necessitated a rate of pouring much below that for the normal foundry practice, and where 2 ingots were poured from 1 pot the cooling in the crucible of the metal for the second ingot was appreciable. This difficulty was overcome by using tapered molds and thus greater certainty as to sound ingots was procured.

V. O. HOMERBERG

Aluminium die-castings. F. A. LIVERMORE. *Chem. Met. Eng.* 25, 664(1921).—Al die-castings not exceeding 1 in. in any direction can be cast with an accuracy of 0.0005 in., the resultant castings possessing smooth surfaces, which can be polished without intermediate machining. Cr-V steel is generally used to die-cast Al, although in some cases cast-Fe dies are used for castings of simple design. The proper venting and gating of the dies are very important. The solvent action of the alloy on the Fe contg. pot and the die must not be too great. Overheated Al dissolves Fe very rapidly. The elongation of the metal is of vital importance in detg. the die-casting properties of an alloy. The Zn-base alloys are not suitable for casting in metal molds, for they absorb Fe from the molds and show a striking tendency to red-shortness. An alloy of 92 Al, 7 Cu and 1 per cent Mn gives very good results for die-casting under pressure. Consideration is given to the die-casting operation, together with a discussion as to the proper temps. to be used and the manner of manipulation. V. O. HOMERBERG

Electrolytic corrosion of thallium-lead alloys. COLIN G. FINK AND CHARLES H. ELDREDGE. *Trans. Am. Electrochem. Soc.* 40, preprint(1921).—Several series of alloys with Pb + Tl as base were investigated as to resistance to corrosion and mechanical properties. The alloys were cast into anodes and submitted to electrolytic corrosion in an acid CuSO₄ soln. contg. both HCl and HNO₃. Tl is one of the few metals whose lower oxide is more stable than the higher oxide; another distinctive feature of Tl is that when alloyed with Pb the fusion curve rises decidedly above that of either constituent, whereas the m. p. of most other binary Pb alloys is lower than that of at least one of the constituents. A minimum anodic corrosion loss of 1.2 lbs. per 100 lbs. of Cu deposited at the cathode resulted with a Pb anode contg. 10% Tl, 20% Sn, balance Pb, as against 65 lbs. loss for ordinary Pb anodes. In general, it was found that Pb-alloy anodes with high m. ps. are more resistant to corrosion. The low corrosion losses are largely due to a very dense, adherent, protective film formed during the very first stages of electrolytic corrosion. C. G. F.

Corrosion of condenser tubes. O. LASCHER. *Z. Metallkunde* 12, 160-78(1920).—L. believes that ordinary chem. corrosion, wearing away of the tube by sand in the water or erosion due to the too rapid passage of steam may be easily detected and prevented. His work, which is in the nature of a preliminary report of the German Corrosion Com-

mittee, deals with the more obscure causes of corrosion: (1) Stray currents are a very frequent and difficultly controlled cause of corrosion. (2) Local pitting or dezincifying is another common phenomenon due to the formation of local galvanic cells owing to the existence of impurities in the metal or an original duplex structure. Section 3 of the paper deals in some detail with the Cumberland process of protection by means of an imposed current from an external source and with other methods of elec. protection. Photomicrographs, drawings and diagrams are given.

R. S. WILLIAMS

Rust prevention by slushing. H. STYRI. *Trans. Am. Electrochem. Soc.* 40, preprint (1921).—Description of a series of tests carried out at the S. K. F. Research Lab., Philadelphia, on the prevention of rusting of steel ball-bearings after covering with a slushing grease. Great cleanliness was required before slushing; this was best obtained by thoroughly cleaning of the steel parts by an aq. soln., preferably by an oil emulsion which leaves a thin oil film for a short time.

C. H. ELDRIDGE

Hyde welding process. ANON. *Engineering* 112, 338-9 (1921).—This process consists essentially in uniting the surfaces by means of molten Cu. It differs from brazing in the fact that the Cu impregnates the masses of the metal to be joined and unites them in such a way that they cannot again be sepd. by heat. The method is usually carried out simply by placing together the pieces to be joined with a small piece of Cu wire or strip adjacent to but not between the joint and then raising the whole to the m. p. of Cu while surrounded by an atm. of H. A further discussion, supplemented by photomicrographs, is given.

V. O. HOMMERBERG

Chloridizing ores and recovery of their metal values. E. A. ASHCROFT. U. S. 1,388,086, Aug. 16. Ores such as Pb or Zn concentrates are treated with mixt. of MgCl₂, CaCl₂, KCl or NaCl, to convert metal of the ore into chloride and the metal of the latter is pptd. by the action of an alloy of heavy and light metals such as Pb or Zn and Mg which are electrolytically regenerated.

Preventing rusting of iron or steel. L. S. CHADWICK and M. RESEK. U. S. 1,388,325, Aug. 23. Fe or steel surfaces are rendered resistant to oxidation by treating them with a soln. formed of Cu phosphates or other phosphates of metals less basic than Fe.

Cleaning metals. J. H. GRAVELL. U. S. 1,387,845, Aug. 16. Fe and steel or similar metals are cleaned by subjection to the action of an etching acid such as H₃PO₄ in the presence of C₂H₆ which serves to remove oil from the metal. Alc. or acetone also may be used.

Shaking apparatus for bag metallurgical fume filters. J. E. PEDERSEN. U. S. 1,388,294, Aug. 23.

Annealing acid-pickled articles. P. A. MEEHAN. U. S. 1,388,188, Aug. 23. Acid-pickled articles of metal which are carried on metal supports during annealing are supplied with acid-neutralizing material such as whitewash which is applied as a coating to the supports. This treatment serves to prevent corrosive action from residual acid or fumes.

Mold for ingots or other heavy steel castings. R. VILLAGE. U. S. 1,388,534, Aug. 23. The feeder head of the mold is provided with a renewable refractory lining.

Vanadium steel for tools. P. A. E. ARMSTRONG. U. S. 1,388,157, Aug. 23. Impact tools for hot work are made of air-hardening alloy steel contg. C 0.30-0.60, Mn 0.30-1.00, Cr 1.00-1.75, Ni 5-6% and the greater part of the remainder Fe.

Casting steel ingots. F. E. MCKENNA. U. S. 1,387,792, Aug. 16. Crucible steel ingots are formed by teeming metal to fill the ingot mold, adding neutral fluxing material such as anhyd. borax before complete solidification of the metal and then teeming a second portion of like metal providing a sink head united with the first metal by the action of the flux. This serves to prevent "pipes" in the metal.

Aluminium-silicon alloy. A. PACZ. U. S. 1,387,900, Aug. 16. An alloy from which machinable castings (suitable for use as internal-combustion engine parts) may be formed is composed of Si 8-20% and Al about 92-80%. Small amts. of other constituents may be present, such as are found in com. Si. The alloy has a sp. gr. of less than 2.7.

Nickel-zirconium alloy. N. PERNOT. U. S. 1,387,663, Aug. 16. In forming an alloy of Ni and Zr, Ni is melted in an elec. furnace and Zr is then combined with the Ni by adding ZrO_2 and Al.

10—ORGANIC CHEMISTRY

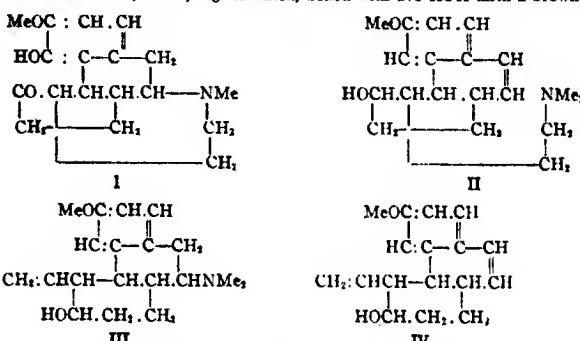
CHAS. A. ROUILLER

A partial synthesis of homocincholoipon and some cyclopentane trione derivatives. ERNST KOENIG AND WALTER OTTMANN. Ber. 54B, 1343-50 (1921).—K. and O. succeeded some time ago in synthesizing homocincholoipon (A) from β -collidine (B) (which they prep'd. by distg. cinchonine with KOH) but delayed publishing their results in the hope of being able to synthesize B also and thus getting around the tedious method of prep'g. it and obtaining it in larger amts. This they have not been able to do. In the present paper they describe some compds. which they obtained in their efforts to carry out the synthesis. When 25 g. B is cautiously treated with 0.5 g. $ZnCl_2$ and 30 g. chloral, heated on the H_2O bath to dissolve the cryst. mass which seps. (probably a polymerization product of the chloral) and allowed to stand 5 days at 35° and the resulting dark brown, thick sirupy oil is freed from most of the chloral and B by vigorously kneading with a little Et_2O , then extd. with 5% HCl, boiled with charcoal, treated with soda, repeatedly extd. with Et_2O and evapd. there is obtained 12 g. chlorocollidine (α -ethyl- β -hydroxy- γ,γ,γ -trichloro- α -propylpyridine) (C), 6-cornered tables from alc., m. 137° , easily sol. in dil. mineral acids; hydrochloride, rhombic tables, m. 105° ; chloroaurate, long yellow tables from concd. HCl, m. 173° . Heated 2 hrs. at 60° with alc. KOH, filtered, concd. *in vacuo* at the lowest possible temp., taken up in a little H_2O and treated with a slight excess of 50% AcOH, 4 g. C gives 1.8 g. β -[β' -ethyl- γ' -pyridyl]acrylic acid (D), fine needles from alc., m. 247° , easily sol. in dil. mineral acids, instantly decolorizes alk. $KMnO_4$ and Br water; hydrochloride, needles, m. 176° ; chloroaurate, narrow yellow prisms, m. 202° . Treated in the least possible amt. of $CHCl_3$ containing a little AcOH with 1 g. Br 1 g. of D gives α,β -dibromo- β -[β' -ethyl- γ' -pyridyl]propionic acid, cryst. powder from Me_2CO , m. 148° . D (1 g.) in 250 cc. hot AmOH quickly treated with 10 g. Na, then, when the reaction is ended, with somewhat less than the calcd. amt. of HCl, freed from the AmOH (together with the bases formed by decomprn.) with steam, strongly acidified with HCl, again distd. with steam, evapd. *in vacuo*, extd. with much hot alc., filtered from the NaCl, again evapd. *in vacuo*, boiled 15 min. with dil. HCl to decompr. any ester formed, decolorized with a little charcoal and concd. gives A.HCl, converted into the chloroaurate (1.4 g.), yellow leaflets, m. 178° , which, treated in much H_2O 3 hrs. with H_2S , then shaken 2 hrs., filtered, evapd. *in vacuo*, freed from the HCl with Ag_2CO_3 and concd. in a desiccator yields the free A, needles, m. 235° ; the oily ethyl ester hydrochloride gives a yellow cryst. chloroaurate, m. 123° . $MeCOPr$ (20 g.) and 34 g. (CO_2Et), treated in ice with 5.4 g. Na in 60 cc. alc., then at once again with the same amts. of (CO_2Et), and NaOBt, heated 10 min. on the H_2O bath, freed from the Na by pptg. with HCl gas, concd. *in vacuo* to about 100 cc. and allowed to cryst. in a desiccator give 42 g. ethyl- β -ethyl- γ -cyclopentanetrione-5-oxalate, stout yellow prisms, m. $120-1^\circ$, sol. in alkalies with dark red color, hydrolyzed by boiling 10 min. with 5 N HCl to the free acid, yellow needles, m. 185° , which, boiled 1 hr. under a reflux with concd. HCl, gives 80% of 3-ethyl- γ -cyclopentanetrione, fine needles with 2 H_2O ,

m. 96° and (anhydrous) softens 68°, m. 173°, (foaming), is hygroscopic, easily sol. in aq. alkalies; monoxime, from 1 g. of the trione in 10 cc. H₂O, 0.4 g. NH₂OH.HCl and 7 cc. of N NaOH, fine needles from H₂O, m. 140°. CHAR. A. ROUILLET.

CHAR. A. ROUILLET

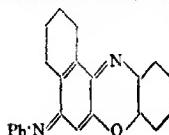
Reduction of dihydrothebainone. EDMUND SPEYER AND SIGURD SIEBERT. Univ. Frankfurt a. M. *Ber.* 54B, 1519-31(1921).—When 20 g. dihydrothebainone (**I**), obtained by the catalytic hydrogenation of thebaine (*C. A.* 15, 1817), in 300 cc. 5 *N* H_2SO_4 is electrolyzed at H_2O -cooled Pb electrodes (*Tafel, Ber.* 33, 2209(1900)) with 12 v. and 8-10 amp. per sq. dm. until the ppt. produced by caustic alkalies is insol. in the latter, then filtered and ptd. with excess of $NaOH$ there is obtained about 70% of a compd. in which the CO group of **I** has been reduced to $CHOH$ and the HO group replaced by H and which is designated *dihydrothebacodine* (**A**); it seps. from $EtOH\cdot H_2O$ in a cryst. meal of prismatic columns with 0.5 H_2O , m. 149°. *Methiodide*, needles, m. 151-2°. *Methiodide* scales, 2 g. of which boiled with 1:1 KOH until a brown oil



seps., yields a *des-N-methyl*dihydrohebacodine (II or III), needles from EtOH-H₂O, m. 147-50°, which with excess of MeI forms a *methiodide* showing no tendency to cryst. and yielding on long boiling with 1:1 KOH much NMe₂, and a compound, probably IV, needles from dil. AcOH, m. 109-10°. When 12 g. A in 75 cc. dry CHCl₃ is slowly added to 8 g. PCl₅ in cold CHCl₃, allowed to stand 2 hrs., boiled under a reflux until no more HCl is evolved (usually about 2 hrs.), poured into 0.5 l. dry Et₂O (which produces an amorphous, exceedingly voluminous ppt.), filtered and heated on the H₂O bath with concd. soda until the oil sepg. at first becomes cryst. there is obtained *chlorodihydrohebacodide* (B) (A in which the HO of the CHO group is replaced by Cl), columns from alc., m. 132°; *methiodide*, m. 240-1° (decompn.). When 2.5 g. B rubbed to a thin paste with 3 cc. 'ubs. alc. is treated with a few pieces of Na, boiled a short time after the reaction has ceased, then, when all the Na has dissolved, treated hot, drop by drop, with H₂O until a faint turbidity appears, there is obtained *desoxydihydrohebacodine* (C) (B in which the Cl is replaced by H), golden yellow leaflets from EtOH-H₂O, sinters 137-8°, m. 146°; *hydroiodide*, elongated columns from H₂O, sinters 250°, decompns. 252°; *methiodide*, stout rhombic columns from H₂O, sinters 264°, m. 268-7°, 2 g. of which, in 10 cc. H₂O, boiled with 1:1 KOH until the pptd. oil is yellow-brown, gives 1.5 g. *des-N-methyl**desoxydihydrohebacodine* (II or III with H instead of HO), columns with 1 EtOH from EtOH-H₂O, m. 132-3°; *methiodide*, oil from H₂O, solidifies on long standing and addition of 1-2 drops alc., m. 261-2° and on boiling with KOH gives NMe₂ and a compound (IV with H instead of Cl), m. 98-9°, insol. in alkalies. The alk. filtrates from the original ppts. of A, when extd. with CHCl₃, dried with Na₂SO₄, evapd.

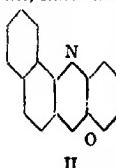
up in alc., treated with concd. HCl in abs. alc. and then with dry Et₂O to incipient turbidity give the *hydrochloride*, columns, decomp. 208° (20 g. from 500 g. thebaine), of *dihydrothebainol* (I with the CO group reduced to CHOH but the phenol HO group still intact), columns with 0.5 H₂O from EtOH-H₂O, sinters 138°, decomp. 142°, easily sol. in caustic alkalies, repptd. unchanged by NH₄Cl. *Hydroiodide*.—*Methiodide*, long 6-sided columns from alc., m. 280°, gives with boiling KOH the *potassium salt*, oil solidifying on cooling, of *des-N-methylidihydrothebainol*; the free base seps. from the aq. soln. of the salt on treatment with CO₂ as fine oil droplets decompd. by atm. O₂ but giving a *hydroiodide*, stout 6-sided columns from H₂O, m. 179–80°; and a *methiodide*, elongated columns from 96% alc., m. 281–2°, which with boiling KOH evolves NMe₂ but the N-free decompn. product could not be obtained cryst.; *methyl ether*, from the base in dil. KOH shaken with Me₂SO₄, quadratic leaflets from alc., sinters 181°, m. 188°, forms a *methiodide*, feathery roddlets from H₂O, m. 284–5°. C. A. ROUILLER.

Synthesis of *oxazines* and *thiazines* of the naphthalene series. I. ZDENKA LUDWIG-SMELIC. *Rev. chim.* 1, 3–6, 23–5, 40–2 (1921).—7,12-Naphthophenoxazine (β,α -form) has been prepd. by condensing 1-amino- β -naphthol with α -aminophenol, and has been identified as the by-product which is formed in the prepn. of α,β -naphthophenoxazine from 1,2-C₁₀H₈(OH)₂ and α -aminophenol. Both isomerides possess the property of passing into oxonium salts when subjected to the action of oxidizing agents in acid soln., and in this respect they resemble the corresponding thiazones, β,α - and α,β -naphthophenothiazines (obtained by the action of S on the corresponding anilino-naphthalenes), which in similar circumstances yield thionium salts. In all 4 cases 2 series of salts are formed, in one of which the org. residue occurs as a univalent and in the other as a bivalent ion. The univalent salts are yellow or red, and the bivalent salts blue or violet. When β,α -naphthophenoxazine is oxidized in alc. or AcOH by FeCl₃, β,β,α -naphthophenozaone is obtained; similarly, β,α -naphthophenothiazine on oxidation yields the corresponding thiazone. The α,β -derivs. do not exhibit this property. If the oxidation of β,α -naphthophenoxazine is conducted in the presence of an aniline salt the product is the corresponding β,α -naphthophenoxazine-5-anil (I). At least two nitro derivs. are formed when β,α -naphthophenothiazine is nitrated. One of these, a *nitrosulfoxide*, may be directly



I

crystd. from the crude nitration product. The other is apparently a *dinitro derivative*, since on reducing the crude product with SnCl₄ and HCl and oxidizing the pptd.



II

stannochloride by means of FeCl₃, there is obtained a *diaminonaphthophenothiazonium chloride*. β,α -Naphthophenoxazine (II), prepd. by heating at 260° 2,1-C₁₀H₈(OH)NH₂·HCl with α -aminophenol, forms lustrous yellow plates, m. 100° (decomp., 107°) in a sealed tube filled with CO₂. It can be sublimed. The alc. soln. shows an intense green fluorescence. The pale blue soln. in H₂SO₄ is colored intensely blue by a trace of H₂O₂, the color being changed to red by addition of ice water. J. C. S.

Dihydrothebaine, dihydrothebainone and dihydrothebainol. A. SKRIBA, with F. F. NORD, J. RÜCKER AND P. STUKART. Univ. Freiburg i. Br. *Ber.* 54B, 1560–4 (1921); cf. Freund and Speyer, *C. A.* 15, 1317.—F. and S.'s dihydrothebaine was obtained in 1913 (Nord, *Diss. Karlsruhe* 1913) by shaking 10 g. thebaine·HCl in H₂O with 20 cc. colloidal Pd soln. (0.04 g. Pd) and H under 1 atm. excess pressure for 30 min.; it seps. from AcOEt in crystals with $[\alpha]_D^{20} -266.86^\circ$ (C₄H₆) and forms only one methiodide, needles from alc., m. 257°. *Acid citrate*, C₈H₁₁O₆N, crystals from C₄H₆·EtOH, decomp. 88–90°. When 33 g. thebaine·HCl in 150 cc. colloidal Pt soln. (1 g.

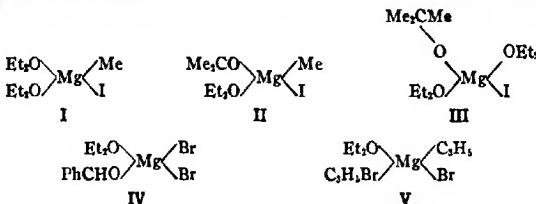
Pt) is shaken with H under 3 atm. excess pressure it absorbs the calcd. amt. of H (4.8 l.) in 1.5 hrs. and another 1.5 l. in 2 hrs. longer and there is formed, together with the alkali-insol. tetrahydrothebaine, m. 143–4°, an alkali-sol. base m. 150–3° yielding an oxime m. 250°. This base, dihydrothebainone, is the sole product when 10 g. thebaine in twice the calcd. amt. of AcOH is shaken with 25 cc. PdCl₂ soln. (0.15 g. Pd) and H under 3 atm. pressure; regenerated from either the HCl salt or the oxime and recrystd. to const. m. p., it m. 137–8° (F. and S. give 150–1°), $[\alpha]_D^{20} -80.12^\circ$ (alc.); methiodide m. 116° (F. and S., 150°); F. and S.'s base was a mixt. of dihydrothebainone with a base richer in H, as indicated by their analytical results (70.82–71.17% C instead of 71.7%) and by the fact that the crude base, m. 150–3°, when not purified through the HCl salt or oxime, gives, together with the methiodide m. 116°, a small amt. of another higher melting methiodide. This base richer in H, *dihydrothebainol*, is obtained by shaking 5 g. dihydrothebainone in 150 cc. H₂O and 40 cc. concd. HCl with 40 cc. H₂PtCl₆ soln. (1 g. Pt) and H under 3 atm. excess pressure for 30 min., making alk. with NH₃·H₂O and extg. repeatedly with Et₂O; it seps. from AcOEt in fine needles, m. 165°, $[\alpha]_D^{20} -36.5^\circ$ (alc.); methiodide, m. 273°; bisphenylurethan, m. 175°. CHAS. A. ROUILLER.

Recent advances in science—Organic chemistry. O. L. BRADY. Univ. London. *Sci. Progress* 16, 195–8(1921); cf. *C. A.* 15, 3271.—Review devoted to new types of isomerism and to org. compds. of As. JOSEPH S. HEPBURN

Pseudo-bases. III. Dialkylaminomethyl alkyl ethers and sulfides. C. M. McILROY AND GERTRUDE M. ROBINSON. Univ. Liverpool. *J. Chem. Soc.* 119, 1470–6 (1921); cf. *C. A.* 12, 141.—The aminomethyl alc. derivs. which result from HCHO and sec. bases condense with alc. and mercaptans, yielding ethers and thioethers. They are mobile oils, distg. without decompn., and rapidly hydrolyzing with dil. HCl. In prepq. these, the sec. amine was gradually added to the aq. 35% HCHO with cooling, the alc., glycol or mercaptan added in 1 portion and the soln. satd. with K₂CO₃. *Diethylaminomethyl ethyl ether*, Et₂NCH₂OEt, from 55 g. Et₂NH, 85 g. HCHO and 40 g. EtOH in 37-g. yield, b₂₀ 136°. *Propyl ether*, by using 61 g. PrOH (yield 58 g.), b. 152–5°. *Isobutyl ether*, by using 74 g. iso-BuOH, in 67-g. yield, b₂₀ 165°. *Isoamyl ether*, by using 88 g. iso-AmOH, in 91-g. yield, b₂₀ 186°. *Di[diethylaminomethyl] trimethylene ether*, from 20 g. Et₂NH, 23 g. HCHO and 9.5 CH₂(CH₂OH)₂, in 28.3-g. yield, b₂₀ 148°. *Tri[diethylaminomethyl] glyceryl ether*, C₁₈H₃₄O₄N₂, prep'd. by gradually treating a mixt. of 12 g. C₂H₅(OH)₂, 22 g. Et₂NH and K₂CO₃ cooled in ice with 30 g. HCHO, K₂CO₃ being added to maintain a satd. soln., b. 162°. *1-Ethoxymethylpiperidine*, C₈H₁₇ON, prep'd. by adding 20 g. HCHO to a mixt. of 20 g. C₂H₅N and 45 g. EtOH, b₂₀ 178–8°. *1-Isobutoxy derivative*, b₂₀ 203°. *Diethylaminomethyl ethyl sulfide*, from 7 g. Et₂NH, 10.6 g. HCHO and 7.7 g. EtSH, in 9-g. yield, b₂₀ 174–5°. *Isopropyl derivative*, b₂₀ 185°. *β-Diethylaminopropiophenone*, BzCH₂CH₂NEt₂, prep'd. by boiling 12 g. BzMe and 16 g. Et₂NCH₂OCH₂CHMe₂ in 50 cc. iso-BuOH for 1 hr., oily. *Picrate*, triangular microcrystals, m. 164°. *Chloroplatinate*, pale brown microneedles. *2,4-Dinitro-β-diethylaminobenzene*, (O₂N)₂C₆H₄CH₂NEt₂, from 11 g. MeC₆H₄(NO₂)₂ and 11 g. Et₂NCH₂O(CH₂)₂CHMe₂, in 30 cc. iso-AmOH; *picrate*, prisms, m. 164°. *Chloroplatinate*, yellow needles. C. J. WEST

Catalytic splitting of allyl alcohol: action of various oxides. PAUL SABATIER AND BONASUKE KUBOTA. *Compt. rend.* 173, 212–6(1921).—Blue oxide of W, prep'd. by reducing WO₃ (obtained by pptg. (NH₄)₂WO₄ with HNO₃, washing and dehydrating below 400°) with H at 350° was the most active catalyst of the oxides investigated. At 350° there was a regular evolution of gas of d. 1.34 consisting of C₂H₄ 73.5, C₃H₆ 10, CO₂ 3, and CO 13% by vcl. 2 vols. H₂O are formed to 1 of supernatant liquor consisting of C₂H₅OH (A), H₂O, CH₂:CHCHO (B), MeCH₂CHO (C), and a small vol. of higher unsatd. aldehydes. A considerable amt. of voluminous C is deposited

of the type I. Similarly, the Friedel and Crafts reaction can best be explained on the assumption of the intermediate formation of complexes in which Al functions with a coordination number of 4.



CHAS. A. ROUILLER

Transformation of acids and their derivatives into aldehydes. A. MAILHE. Toulouse. *Caoutchouc & gutta-percha* 18, 10793-6(1921).—A description of the work of Sabatier, de Godon, Rosenmund, Zetsche and M. on the reduction of aliphatic acids and acid anhydrides, and of aliphatic and aromatic acid chlorides to their corresponding aldehydes by TiO₂, Ni, Pd and similar catalysts. No new research is reported.

C. C. DAVIS

Labile nature of the halogen atoms in substituted nitromethanes. A. K. MACBETH AND D. D. PRATT. Univ. St. Andrews. *J. Chem. Soc.* 119, 1356-61(1921).—In the case of most substituted nitromethanes, the reaction with alk. N₂H₄ is quant. and may be used to estimate the amt. of the different NO₂ compds. in soln. Two mols. C(NO₂)₃Cl react to give 2 (NO₂)₂CK, 2 KCl, N₂ and 4 H₂O. Thus, the Cl atom is labile. C(NO₂)₃Br decompd. N₂H₄ in the same way. In neither case is there a reduction of NO₂ to NH₂. The same reaction takes place with CBr₃(NO₂)₂, CCl₃(NO₂)₂ and PhCBr(NO₂)₂, but not with CH₃BrNO₂. The results indicate that the presence of the NO₂ group in the halogen derivs. of CH₃ renders the halogen atom more labile than it is in the case of the alkyl halides. The effect is more pronounced when several NO₂ groups are present, since (NO₂)₃CBr₃ and (NO₂)₃CBr part with their Br in the cold, whereas BrCH₃NO₂ is only broken down on heating. The presence of other electronegative groups enhances the effects of the NO₂ groups. A certain parallel may be drawn between the behavior of the poly-NO₂ aliphatic compds. and the poly-NO₂ aromatic compds., especially those in which the *o,p*-influence of the NO₂ groups exists; in neither case does reduction of the NO₂ group to an NH₂ group occur, but in both replacements take place. The effect of the NO₂ group in increasing the lability of halogens in the aliphatic series becomes more marked when the action of N₂H₄ on such substances is contrasted with the negative results obtained in the case of other halogen derivs. C. J. WEST

Colorations produced by substituted nitroforms. HUGH GRAHAM AND A. K. MACBETH. Univ. St. Andrews and Queen's Univ. *J. Chem. Soc.* 119, 1362-8(1921); cf. *C. A.* 9, 612, 1037.—A spectroscopic examn. has been made of BrC(NO₂)₃ and ClC(NO₂)₃, as well as Br₂C(NO₂)₂ in alc., and in the presence of different influencing substances, such as piperidine, MeNH₂, carvene, Et₂S, EtSH, (CH₃)₂S. The 1st 2 in CHCl₃ and alc. show general absorption only. The form of the curve indicates that in alc. BrC(NO₂)₃ exists in part in the *ac*-form. The Cl compd. does not show the same degree of tautomerization. Piperidine produces a pronounced yellow color and shifts the bands from the region of λ2800-3000 to λ2800. These colors are probably due to the breakdown of these substances to the piperidine and other salts of CH₃(NO₂)₃ which have the conjugated *ac*-structure. The colors with Br₂C(NO₂)₂ are very faint, which may be explained by its slow reduction. C. J. WEST

The reaction of taurine with α -naphthyl isocyanate. C. L. A. SCHMIDT. Univ. California. *Proc. Soc. Exptl. Biol. Med.* 18, 204–5 (1921).—Taurine, like the NH_2 carboxylic acids, reacts with $\alpha\text{-C}_8\text{H}_7\text{NCS}$ to yield the corresponding hydantoic acid. The Ba salt of α -naphthylureidoethylsulfonic acid was prepd. by a method described.

V. C. MYERS

Quantitative studies of the action of amino acids on sugars. L. GRÜNHUT AND J. WEISER. Deut. Forschungsanstalt Lebensmittelchemie, München. *Biochem. Z.* 121, 109–19 (1921).—When 0.005 g.-mol. of an NH_2 acid and a like amt. of sugar are dissolved in 200 cc. CO_2 -free H_2O and the reaction process after evapn. is studied by means of the formol titration, polariscope and Fehling reduction test, it is found that the reaction capacity decreased with increasing mol. wt. The reaction of glycocoll, alanine, leucine, aspartic acid and glutamic acid with various mono- and disaccharides was studied. Glutamic acid, of the NH_2 compds., and a pentose (*D*-arabinose), of the sugars, are the most reactive. The study as a whole indicates a wide difference in the interaction of the various compds. used. No tables are given. F. S. HAMMETT

Condensation of chloroacetic ester with magnesium in the presence of acetic ester. MARCEL SOMMELET AND J. F. HAMEL. *Bull. soc. chim.* 29, 545–53 (1921).—In Et_2O , PhH , or CHCl_3 , $\text{CICH}_2\text{CO}_2\text{Et(A)}$ and Mg activated with HgCl_2 give only $\text{CICH}_2\text{COCH}_2\text{CO}_2\text{Et(B)}$, according to the scheme: A + $\text{CIMgCH}_2\text{CO}_2\text{Et} \rightarrow \text{CICH}_2\text{C(O}\text{MgCl)}\text{(OEt)}\text{CH}_2\text{CO}_2\text{Et} \rightarrow \text{B}$, but in the presence of Et_2OAc the chief product is $\text{AcCH}_2\text{CO}_2\text{Et(C)}$. While this may be interpreted: $\text{AcOEt} + \text{CIMgCH}_2\text{CO}_2\text{Et} \rightarrow \text{MeC(O}\text{MgCl)}\text{(OEt)}\text{CH}_2\text{CO}_2\text{Et} \rightarrow \text{C}$, it is also possible that the Et_2OAc does not enter into the reaction and that C is formed by the action of H_2O on $\text{CIMgCH}_2\text{COCH}_2\text{CO}_2\text{Et}$. It was attempted to settle this question by using Et isovalerate, but only minute amounts of a β -ketonic ester b.p. 104–6° could be obtained. Next, the action of BzCl was investigated; 62 g. A, 88 g. EtOAc , and 12 g. Mg were condensed in Et_2O , cooled, and treated drop by drop with BzCl , finally heating 2 hrs. on the H_2O bath. After pouring on ice, acidifying with H_2SO_4 , and extg. with Et_2O , the Et_2O is washed with 10% aq. KHCO_3 to remove BzOH , dried, concd. and fractionated *in vacuo*. The 1st fraction consists of BzOEt , formed as follows: $\text{MeC(O}\text{MgCl)}\text{(OEt)}\text{CH}_2\text{CO}_2\text{Et} + \text{BzCl} \rightarrow \text{BzOEt} + \text{C} + \text{MgCl}_2$. The higher boiling fractions consist of mixts. of 2 β -ketonic esters which were sepd. (not in every trial) by conversion into the Cu derivs. with satd. aq. Cu(OAc)_2 and fractionating from PhH . The more sol. is yellow-green, m. 172°, and is identical with the Cu deriv. of $\text{BzCH}_2\text{CO}_2\text{Et(D)}$, which is formed as follows: $\text{BzCl} + \text{CIMgCH}_2\text{CO}_2\text{Et} \rightarrow \text{D} + \text{MgCl}_2$. The second Cu deriv. is blue, m. 224°, and corresponds to that of $\text{AcBzCHCO}_2\text{Et(E)}$, whose formation would be due to the presence of the deriv. $\text{AcCH}(\text{MgCl})\text{CO}_2\text{Et}$. It is, therefore, concluded that the Et_2OAc actually enters into the reaction; otherwise $\text{BzCH}_2\text{COCH}_2\text{CO}_2\text{Et}$ would have been observed. E was also prepd. according to the method of Bouveault and Bonert (*Bull. soc. chim.* [8] 27, 1044 (1902)): 32.5 g. C are added to 175 g. Et_2O and 6 g. Na wire, and when soln. is complete, the calcd. amt. of BzCl , in small portions with shaking. After heating on the H_2O bath until a test portion treated with water no longer reacts acid to litmus, decompn. with H_2O , and extn. with Et_2O , the C-Bz deriv. is extd. by the slow addition of 8% NaOH , set free with dil. HCl , freed from the accompanying BzOH by taking up in Et_2O and shaking out with 10% Na_2CO_3 , and fractionated. C passes over first, then E, b.p. 160–70°.

M. HEIDELBERGER

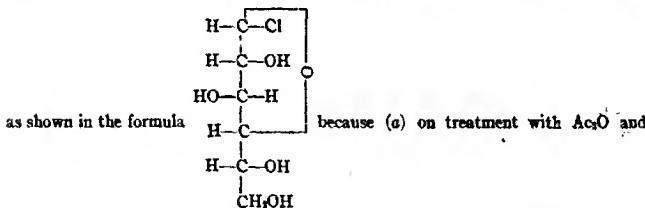
Condensation of esters with esters of α -bromo acids in the presence of zinc. Ethyl γ -ethoxyacetacetate. MARCEL SOMMELET. *Bull. soc. chim.* 29, 553–65 (1921); cf. C. A. 6, 1603; also Johnson *et al.*, C. A. 7, 2224; 8, 3295; 10, 2732; Fosse and Laude, C. A. 15, 3272.—A more extended discussion is given than in the preliminary articles. New observations are: $\text{EtOCH}_2\text{COCH}_2\text{CO}_2\text{Et}$, d₄¹⁷ 1.047, forms a phenylpyrasolone,

EtOCH₂C(N.NPh.CO.CH₃)₂, when heated 4 hrs. at 100° with PhNNNH₂ in alc., alc., m. 82-3°.

EtOCH₂COCH(CH₂Ph)CO₂Et, d_4^{15} 1.073, saponified with alc. KOH, gives PhCH₂CH₂COCH₂OEt, d_4^{15} 1.017, purified through the bisulfite compd. BrCH₂CO₂Et reacts similarly with MeOCH₂CO₂Et (A), iso-BuOCH₂CO₂Et (B), and PhOCH₂CO₂Et (C), forming β -ketonic esters characterized by their copper derivatives: that from A forms green needles from C₆H₆; that from B crystals from aq. alc., m. 96°; that from C seps. as green crystals from C₆H₆-petr. ether, m. 16-23°. M. HEDRICK

Passage from guanidine to cyanamide and from diguanide to dicyanodiamide. GURU PELLIZZARI. *Atti accad. Lincei* 30, I, 171-5 (1921).—By the addition of NH₂OH (1 mol.), cyanamide is converted into guanidine and dicyanodiamide into diguanide. The only known reaction occurring in the opposite sense is the transformation of *o*-phenylenediguanide into *o*-cyano-*o*-phenyleneguanidine by treatment with HNO₃ (C. A. 15, 1533). This treatment has now been extended to other compds., and it is found that HNO₃ converts diguanide into cyanoguanidine or dicyanodiamide, NH[*C*(:NH)NH₂]₂ + HNO₃ = NH₂[*C*(:NH)HCN] + N₂ + 2H₂O, and guanidine similarly yields a small proportion of cyanamide. Although the NH₂ is liberated as N and water, which are the decompn. products of NH₂NO₂, there are indications that the HNO₃ does not directly detach a mol. of NH₂, but that an intermediate compd. is formed. In the case of guanidine, this intermediate compd. has been identified with nitrosoguanidine (cf. Thiele, *Ann.* 273, 133-44) the formation of which represents a reversible reaction, NH₂C(NH₂)₂ + HNO₃ ⇌ NH₂C(NH₂)NHNO + H₂O; the mechanism of the reaction in the other two cases is probably similar. J. C. S.

α -Glucosyl chloride and a new disaccharide (α -glucosidoglucose). AND PIERRE CASTAN. Univ. Geneva. *Helvetica Chim. Acta* 4, 319-24 (1921); cf. C. A. 14, 3226.—In a previous paper it was stated that glucosan dissolves in concd. HCl with a loss of color and that on evapn. of the soln. a syrupy product is obtained which contains Cl. It is now found preferable first to neutralize the HCl soln. with Ba(OH)₂, evapn. on a water bath and then dissolve in cold EtOH; evapn. of the alc. soln. leaves a colorless, vitreous and transparent residue, which could not be recrystd. The reaction is as follows: C₆H₁₀O₆ + HCl = C₆H₁₁O₆Cl. It is a deriv. of glucose in which the Cl has taken the place of an OH group. This glucosyl chloride (A) has the Cl atom



AcONa it is converted into α -acetochloroglucose, m. 63°, and (b) when heated in alc. with NaOMe it yields α -Me glucoside. A dissolves readily in cold H₂O and gives no ppt. of AgCl with AgNO₃ until heated. When glucosan in MeOH is treated with alc. KOH a compd. (B) ppts. in which K replaces the H of an OH group; B is hygroscopic and must be rapidly filtered and washed with Et₂O. It probably has the K on the primary alc. group in the sugar. When equimol. ams. of A and B in 95% EtOH are heated on a water bath, the soln. becomes brown and KCl is pptd. mixed with a resin; when it is boiled 4 hrs., filtered, the alc. removed by distn. and Et₂O added a dark oily ppt. is formed, which was redissolved in H₂O and is probably a glucorylglycoses formed

as follows: $C_6H_{10}O_4Cl + CaH_4O_4K = C_6H_{10}O_4 + KCl$; no attempt was made to isolate the compd. It was hydrated by boiling with animal charcoal, yielding the disaccharide, α -glucosidoglucose (C), $C_12H_{22}O_11$; the crystals obtained by slow evapn. of the H_2O soln. are the monohydrate, m. 90° with loss of H_2O , then m. 187° , readily sol. in H_2O , less sol. in EtOH or MeOH and insol. in Et_2O ; C does not give a red color with fuchsin-SO₄; on warming Fehling soln. is reduced, 1 g. being equiv. to 0.590 g. glucose; when boiled 2 hrs. with HCl it is converted completely into glucose. Its properties are very similar to those of gentiobiose (D) in the bitter taste, the rotation and power to reduce Fehling soln. The rotation of D is first -5° , then finally becomes 10.37° , whereas that of C is first 12.02° , then finally 10.57° ; unlike D, C is not hydrolyzed by emulsin; the osazone from C m. $173-4^\circ$. P. and C. intend to extend this method to the prepn. of other disaccharides.

N. A. LANGE

Syntheses of cyanic acid and urea by oxidation of organic substances: amides, nitriles, methylcarbylamine. R. FOSSE AND G. LAUDE. *Compt. rend.* 173, 318-21 (1921); cf. *C. A.* 15, 1884, 3272.—Although monobasic acids oxidized with KMnO₄ in NH₄OH do not give HCNO (A) or CO(NH)₂ (B), the corresponding amides do. After heating the oxidation product with NH₄Cl, HCONH₂ gives 28% B, while AcNH₂ gives only 1%. B was obtained from (CONH₂)₂ (C) by Hofmeister (*Arch. exp. Path. u. Pharm.*, 37, 426 (1898)). Just as an isocyanic deriv. is the intermediate product in the Hofmann reaction, so in the formation of B from C, HCNO is the precursor of B. C, aq. NH₄, and powdered KMnO₄, after 15 hrs. at room temp., then destroying the excess KMnO₄ on the H₂O bath, give a liquid containing no urea until after heating with NH₄Cl, then containing 4.3 g. per 100 g. C. This may be increased to 12.7 if the oxidation is carried out in the presence of Cu. A is isolated as the Ag salt and characterized by the cobalticyanide and oxyurea tests (HONH₂ and FeCl₃). CH₃(CONH₂)₂ gives 50-67% B after heating the oxidation products with NH₄Cl, depending on whether Cu is absent or present, resp., while (CH₃CONH₂)₂ gives only 1.85%. Nitriles also give rise to A and B more readily than their acids. MeNC yields on oxidation a liquid containing practically no B until heated with NH₄Cl, when 48.2% are found. The results are summarized in a table.

M. HEIDELBERGER

Synthesis of amylopectin by esterification of the erythroamylloses with phosphoric acid. SAMUEL AND (MISS) ANNA MAYER. *Compt. rend.* 173, 321-2 (1921); cf. *C. A.* 8, 837; 15, 3820.—Neuberg's method (cf. Kerb, *C. A.* 14, 2341) was used, resulting in a white flocculent material, insol. in H₂O at 100° but dissolving in a few min. at 120° , gives a violet-brown color with I. This product appears to be a Ca amylophosphate, from which the Ca is removed by "electrodialysis," depositing a very viscous jelly on the membrane. The cond. of a 0.16% soln. is 0.63×10^{-4} , while that of the gel in a concn. of 0.98% is 11.68×10^{-4} . The properties of the product depend somewhat on the amt. of POCl₃ used and the conditions of the expt. A table is given with comparisons of the cond., viscosity, mol. wt. and P₂O₅ content of amylopectin, the erythroamylloses, and the synthetic esters.

M. HEIDELBERGER

Configuration of α,α' -dibromodibasic acids. I. Dibromo adipic acids. Synthesis and resolution of *trans*-cyclopentane-1,2,3-tricarboxylic acid. WILLIAM HENRY PERKIN, JR. AND ERIC ROBINSON. Dyson Perrins Lab. *J. Chem. Soc.* 119, 1392-9 (1921).—*Ethyl cyclopentane-1,2,3,3-tetracarboxylate*, $C_11H_{16}O_8$, was prep'd. by boiling 2.3 g. Na in 50 cc. alc., 16 g. $CH_3(CO_2Et)_2$, and 17 g. $(CH_3CHBrCO_2Et)_2$, in 50 cc. alc. for 20 min., b.p. 214-6°. Digested with 1.5 times the calcd. amt. of MeOH-KOH for 4 hrs., it yields *dl-trans*-cyclopentane-1,2,3-tricarboxylic acid (A), m. $184-5^\circ$, readily sol. in H_2O , much less sol. in HCl. Transformed into the brucine salt, $[\alpha]_D - 20.87^\circ$, the pure *d*-acid is obtained after 6 crystals of the salt from hot H_2O . The *d*-acid m. $125-6^\circ$, has $[\alpha]_D$ 72.4° in H_2O , and is readily sol. in H_2O . When heated with Ac₂O

(8 hrs. at 150°) the *trans*-acid forms the *cis*-acid (B), thick sugar-like crystals from dil. HCl, m. 169–70°, more sol. in HCl or H₂O than the *trans*-acid. A mixt. of equal amts. of the 2 acids m. 145–50°. Because of these reactions it is concluded that A is the *d*-modification, and that B represents the *meso*-modification, and should be obtained from the *meso*-form of the Br₃ acid. Opposite conclusions have been drawn by Ingold (*C. A.* 15, 3078).

C. J. WEST

Resolution of *dl-trans*-cyclopentane-1,3-dicarboxylic acid. WILLIAM HENRY PERKIN, JR. AND HAROLD ARCHIBALD SCARBOROUGH. Dyson Perrins Lab. *J. Chem. Soc.* 119, 1400–8(1921).—This resolution was undertaken in order to compare the rotation of the active acid with that of camphoric acid. The value, 5.86°, is much smaller than that exhibited by *d*-camphoric acid, 49.7°, so that the introduction of 3 Me groups into the mol. has the effect of raising the rotation 44°. This rotation is much smaller than that of any of the other fully satd. acids so far examd. Comparison of the m. ps. shows that the *cis*-acid always melts at a higher temp. than the corresponding *trans*-acid, whereas in the acids of the 1,2- or 1,4-type the reverse is the case. *trans*-Cyclopentane-1,3-dicarboxylic acid (Pospischill, *Ber.* 31, 1951) was synthesized by the use of CH₃Br₂ in place of CH₃I₂. The crude Et cyclopentanetetracarboxylate is extd. twice with Et₂O, the Et₂O soln. washed, dried, evapd., and 50 g. of the resulting oil hydrolyzed by boiling 2 hrs. with 34 g. NaOH in 250 cc. 80% alc. Evapd. with H₂O till free from EtOH, decompd. with 150 cc. concd. HCl, concd. on the steam bath, extd. with Et₂O, and the residue heated at 170–180° till CO₂ evolution ceases, the mixt. of *cis*-anhydride and free *trans*-acid is esterified by boiling with 6 times its wt. of 10% alc. H₂SO₄ for 6 hrs.; on hydrolysis of the esters a mixt. of the 2 acids was obtained. The dried mixed acids are shaken with AcCl and allowed to stand 24 hrs. On rubbing with dry Et₂O the *cis*-anhydride remains undissolved. On further treatment with AcCl, pure *trans*-acid is obtained. The resolution was accomplished by the use of brucine, the *d*-salt crystg. from H₂O as brilliant flat needles, m. 127°, [α]_D –29.54°, contains 9 H₂O, effloresces in a desiccator. Decompd. with NH₄OH, *d*-*trans*-cyclopentane-1,3-dicarboxylic acid is obtained, m. 93–5°, [α]_D 5.86°. Ethyl ester, b.p. 145°, [α]_D 5.01°. The *l*-acid m. 90–3°, [α]_D –5.29°. *cis*-1,3-Dibromocyclopentane-1,3-dicarboxylic acid, C₈H₁₀O₄Br₂, prep'd. by heating 5 g. of the *cis*-acid with 20 g. PCl₅ till HCl evolution ceased, then adding 15 g. Br and heating several hrs. on the H₂O bath, and finally heating with 30 cc. HCO₂H until decompr. was complete, m. 184° (from HCO₂H). Methyl ester, by adding the acid chloride to well cooled MeOH, b.p. 170°. The unsatd. acid could not be prep'd. CH₃I₂ was prep'd. from CH₃Cl₂ by heating 30 g. CH₃Cl₂ and 120 g. NaI in 100 cc. AcMe under pressure for 10 hrs., relieving the pressure and then reheating for 10 hrs. H₂O was added, the product extd. with Et₂O, washed with NaHSO₄ soln. and fractionated, giving 60% CH₃I₂. C. J. WEST

Preparation of trialkyl and triaryl derivatives of iodine. VICTOR ARREGUINE, JR. AND E. D. GARCIA. *Anales soc. quim. Argentina* 9, 121–8(1921).—By Friedel and Crafts' reaction with ICl₄ and C₆H₆ in Et₂O at 0° or lower, Cl-substitution products of C₆H₆ were obtained together with small amts. of PhI; derivs. of tervalent I were not obtained. The reaction was extremely violent and much free I was liberated. Grignard's reaction, using MeMgI with both ICl₄ and PhI, gave equally unsuccessful results. In the case where PhICl₄ was used, PhI and Ph₃I were formed.

L. E. GILSON

Color and optical activity in organic compounds. E. LONGOBARDI. *Anales soc. quim. Argentina* 8, 153–61(1920).—The possibility of an antagonism between optical activity and color in org. compds. is discussed. Colored compds. exist, which, from their structure, should exhibit optical activity. Where optical activity has been verified, certain anomalies occur, and, further, the materials used have been of doubtful purity.

Unsuccessful attempts were made by L. to resolve alkali blue, and nitrotyrosine, obtained from *L*-tyrosine.

L. E. GILSON

The nitro and amino derivatives of *m*-methylethylbenzene. ALPHONSE MAILLER. *Compt. rend.* 173, 160-2 (1921); *Bull. soc. chim.* 29, 713-7 (1921).—*m*-EtC₆H₄Me nitrated in the cold by a mixt. of HNO₃ (1 part fuming) and AcOH (0.5 part glacial) gave a mono-NO₂ deriv., b. 245°, which was identified as the 2,6-Et₂O₂N)C₆H₄Me by its formation of 2,3-Me(O₂N)C₆H₃CO₂H on oxidation with hot dil. HNO₃. The use of sulfo-nitric mixt. yielded a mixt. of NO₂ derivs. together with a dinitro-1,3-dicarboxylic deriv., m. 215°. A MeEtC₆H₄(NO₂)₂ m. 90° resulted when a fuming H₂SO₄-HNO₃ mixt. was used as the nitrating agent. On reduction the mono-deriv. gave 2,6-Et-(H₂N)C₆H₄Me (A), b. 228-9°, a colorless liquid, darkening on contact with air or light. Its hydrochloride, m. 152°, is sol. in water and gives an intense blue color with CaOCl₂. A on being boiled with the resp. org. acid yielded the 1-methyl-3-ethyl-6-substituted amides which follow: formanilide, m. 151°; acetanilide, m. 103°; propionanilide, b. 318-20°; butyranilide, m. 72°; isovaleranilide, m. 68°; benzylanilide, m. 152°. With PhNCO A yielded MeEtC₆H₄NHNHPh, m. 105°. With BzH A gave PhCH₂NC₆H₄Me, b. 330°, and with iso-BuCHO, iso-BuCH:NC₆H₄MeF, b. 268-70°. With glycerol, H₂SO₄ and PhNO₂, there was formed 5-methoxy-7-ethylquinoline, a light yellow liquid, b. 273-5°. By the method of M. and de Godon (cf. *C. A.* 15, 1500) the di-Me deriv. of A was prepnd., MeEtC₆H₄NMe₂, b. 217°, and likewise the di-Et deriv., b. 235°. Neither compd. formed a salt with H₂SO₄, blackened in air or light, condensed with BzH, or was oxidized by PbO₂.

R. L. BROWN

Arylhydroxylamines and arylazides—a parallel. EUGEN BAMBERGER. Zürich. *Ann.* 424, 233-66 (1921); cf. *Ber.* 33, 3800 (1900); *C. A.* 1, 2109, 2110.—B. shows, in the 1st 13 pages, that most of the reactions of R'NHOH may be explained equally well whether one starts with the formula R'NHOH, or assumes that the compd. dissociates into H₂O and R'N. The hypothesis is useful in explaining the transformation into MeOC₆H₄NH₂ and into X(MeO): C₆H₄. O. The remainder of the paper is devoted to a comparison of the reactions of R'NHOH and R'N₂, since Friedländer and Zeitlin (*Ber.* 27, 192; 28, 1386) have assumed that in the transformation of PhN₃ into HOCH₂NH₂, the intermediate product is PhNHIOH. The conclusion is that the assumption is probably incorrect, because (1) the same product is not obtained in each case from the 2 classes of compds. and (2) the same decomprn. products are obtained, even if the azide is decomprd. in the absence of H₂O. B. believes that the explanation of the same decomprn. products lies in the formation of the same intermediate product from each class of compds., namely R'N, R'NHOH losing H₂O and R'N₂ losing N₂ (cf. Goldschmidt and Larsen, *C. A.* 4, 1409, and Stieglitz and Curme, *C. A.* 7, 2397). In the comparative study of the 2 classes, identical conditions were not always used, so that it may be that the qual. as well as the quant. course of the reaction was influenced. No exptl. details are given; most of the work is taken from various dissertations. 20 g. PhNHOH, warmed with dil. H₂SO₄ (1:10) for 45 min. at 98°, gave 14 g. HOCH₂NH₂, 2 g. Ph₂N₂O, and traces of 1,2,4-HO(SO₂H)C₆H₃NH₂; 10 g. PhN₃, boiled 24 hrs. with dil. H₂SO₄, gave several g. HOCH₂NH₂, 6 g. 1,2,4-HO(SO₂H)C₆H₃NH₂, but no Ph₂N₂O. 6 g. PhNHOH, heated 5 min. with PhOH and dil. H₂SO₄, gave 0.9 g. H₂NC₆H₄C₆H₃OH, PhNH₂ and some Ph₂N₂O. 6 g. PhN₃, heated 1.75 hrs. with PhOH and dil. H₂SO₄, gave 0.4 g. H₂NC₆H₄C₆H₃OH, traces of PhNHC₆H₃OH, a little PhNH₂, but no Ph₂N₂O. 100 g. PhNHOH heated with 2400 cc. EtOH and 50 cc. H₂SO₄ for 26 hrs. or allowed to stand at room temp. for 3 months gave 45 g. 4-H₂NC₆H₄OEt, 8 g. 2-H₂NC₆H₄OEt, 3.5 g. each of *p*- and *o*-H₂NC₆H₄OH, 4 g. PbNH₂, 14 g. Pb₂N₂O. 15 g. PhN₃, warmed 25 hrs. with 105 cc. EtOH (mixed with 0.5 vol. H₂SO₄), gave 5.5 g. 4-H₂NC₆H₄OEt, 0.3 g. 2-H₂NC₆H₄OEt, 0.5 g. *p*-H₂NC₆H₄OH, 0.4 g. PhNH₂, but no Ph₂N₂O. With MeOH,

H_2SO_4 and PhNHOH as above, the products were: 21 g. 4- $\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$, 6 g. 2- $\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$, 0.2 g. p - $\text{NH}_2\text{C}_6\text{H}_4\text{OH}$, a little PhNH_2 and 17 g. PhN_2O . 5 g. PhN_2 gave 1.9 g. 4- $\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$, 0.4 g. 2- $\text{H}_2\text{NC}_6\text{H}_4\text{OMe}$ and PhNH_2 , 0.05 g. p - $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$, but no $\text{Ph}_2\text{N}_2\text{O}$. Concd. HCl (satd. at 0°), acting on 80 g. PhNHOH for 30 days, gave 37 g. p - $\text{H}_2\text{NC}_6\text{H}_4\text{Cl}$, 15 g. σ - $\text{H}_2\text{NC}_6\text{H}_4\text{Cl}$, 0.2 g. σ,p - $\text{Cl}_2\text{C}_6\text{H}_4\text{NH}_2$, 0.2 g. $\text{Ph}_2\text{N}_2\text{O}$, while 131 g. PhN_2 gave 86 g. p - $\text{H}_2\text{NC}_6\text{H}_4\text{Cl}$, 25 g. σ - $\text{H}_2\text{NC}_6\text{H}_4\text{Cl}$, 0.3 g. σ,p - $\text{Cl}_2\text{C}_6\text{H}_4\text{NH}_2$, and 0.2 g. PhNH_2 . 34 g. σ - $\text{MeC}_6\text{H}_4\text{NHOH}$ (A), allowed to stand 30 days at room temp. with 1000 cc. MeOH and 17 cc. H_2SO_4 , gave 13 g. 2,4-Me(MeO) $\text{C}_6\text{H}_4\text{NH}_2$ (B), 0.2 g. 2,4-Me(HO) $\text{C}_6\text{H}_4\text{NH}_2$ (C), and 0.7 g. σ -azoxytoluene (D). 20 g. σ - $\text{MeC}_6\text{H}_4\text{N}_2$ (E) treated with 2 vols. EtOH and 1 vol. H_2SO_4 (24 hrs. at room temp. and then warmed) gave 4.8 g. 2,4-Me(EtO) $\text{C}_6\text{H}_4\text{NH}_2$, C, 1.2 g. D, etc. 61 g. A, warmed with 1:10 H_2SO_4 for 45 min., gave 20.4 g. C, 1.3 g. σ - $\text{MeC}_6\text{H}_4\text{NH}_2$, 7 g. D, etc., 30 g. A, treated with concd. HCl for 30 days in the cold, gave 13 g. 2,4-Me $\text{ClC}_6\text{H}_4\text{NH}_2$ (F), about 0.3 g. 2,6-Me $\text{ClC}_6\text{H}_4\text{NH}_2$ (G), about 1 g. 2,5-Me $\text{ClC}_6\text{H}_4\text{NH}_2$ (H), 0.3 d. D, etc. 120 g. E, treated 8 days with concd. HCl , gave 100-110 g. F, some G and H, but no D. 30.7 g. 3-Me $\text{C}_6\text{H}_4\text{NHOH}$ (I), treated with 900 cc. EtOH and 15 cc. concd. H_2SO_4 for 15 days (dark), gave 3.7 g. 3,4-Me(EtO) $\text{C}_6\text{H}_4\text{NH}_2$ (J), very little 3,4-Me(HO) $\text{C}_6\text{H}_4\text{NH}_2$ (K) and 3.4 g. m -azoxy-toluene (L). 10 g. 3-Me $\text{C}_6\text{H}_4\text{N}_2$ (M), treated with 2 vols. EtOH and 1 vol. H_2SO_4 (3 days in the cold, 1.5 hrs. on the H_2O bath) gave 1.4 g. J, 2.5 g. K, but no L. With MeOH , I gave more than 10 g. of 3,4-Me(MeO) $\text{C}_6\text{H}_4\text{NH}_2$ (N), a little 3,4-Me(OH)- $\text{C}_6\text{H}_4\text{NH}_2$ (O), and L. 8 g. M gave more than 1.7 g. N, 2.6 g. O but no L. 3.8 g. 3,6-Me $\text{C}_6\text{H}_4\text{NHOH}$ (P), warmed 35 min. with dil. H_2SO_4 , gave 2 g. 3,6,4-Me $\text{Cl}(\text{HO})\text{C}_6\text{H}_4\text{NH}_2$ (Q), 1.1 g. 3,6,4-Me $\text{Cl}(\text{HO})\text{C}_6\text{H}_4\text{OH}$ (R), and a little p -azoxylxylene (S). 10 g. 3,6-Me $\text{C}_6\text{H}_4\text{N}_2$ (T), warmed 15 hrs. with dil. H_2SO_4 , gave 4.1 g. Q, 2.1 g. R, but no S. 175 g. EtOII and 2.5 cc. H_2SO_4 , acting for 3 days on 5 g. P, gave 1 g. 2,6,4-Me $\text{Cl}(\text{EtO})\text{C}_6\text{H}_4\text{NH}_2$ (U), 1.5 g. S, and a little 2,6,4-Me $\text{Cl}(\text{EtO})\text{C}_6\text{H}_4\text{NH}_2$ (V) and $\text{MeC}_6\text{H}_4(\text{OH})_2$ (W). 15 g. T and a mixt. of 2 vols. EtOH and 1 vol. H_2SO_4 gave 5.2 g. V, 4.6 g. U, 0.5 g. 3,6,4-Me $\text{Cl}(\text{EtO})\text{C}_6\text{H}_4\text{OH}$ and 0.15 g. W. MeOH , H_2SO_4 and P gave nearly the theoretical amt. of 2,6,4-Me $\text{Cl}(\text{MeO})\text{C}_6\text{H}_4\text{NH}_2$, while 5 g. T gave 2.5 g. of this compd. 10 g. p - $\text{ClC}_6\text{H}_4\text{NHOH}$ (X), warmed with 1:5 H_2SO_4 for 25 min. at 40-50°, gave 1.2 g. p - $\text{ClC}_6\text{H}_4\text{NH}_2$ (A'), 0.45 g. 4,6-Cl $\text{C}_6\text{H}_4\text{NH}_2$ (B'), 5 g. p -dichloroazoxybenzene (C'), traces of PhNH_2 , etc. p - $\text{ClC}_6\text{H}_4\text{N}_2$ (Y) gave 0.9 g. A', 0.45 g. B', traces of PhNH_2 , but no C'. 5.5 g. X, warmed 20 min. at 50° with 1:3 HCl , gave 2.4 g. B', 0.7 g. A' and 1.5 g. C'. 5 g. Y, warmed 22 hrs. with dil. HCl , gave 1.8 g. B', 0.45 g. A' but no C'. 10 g. p -Br $\text{C}_6\text{H}_4\text{NHOH}$ and dil. H_2SO_4 gave 0.3 g. 4,6-Br $\text{C}_6\text{H}_4\text{NH}_2$ (D'), 2.4 g. p -Br $\text{C}_6\text{H}_4\text{NH}_2$ (E'), a little 4,6-Br(HO) $\text{C}_6\text{H}_4\text{NH}_2$ (F') and 5 g. p,p' -dibromoazoxybenzene (G'). p -Br $\text{C}_6\text{H}_4\text{N}_2$ gave very little F' and no G', while the wts. of D' and E' were not detd. Boiling 14.5 g. p - $\text{MeC}_6\text{H}_4\text{NHOH}$ with dil. H_2SO_4 for 40 min. gave 9 g. 1,4-(HO) $\text{C}_6\text{H}_4\text{Me}$ (H'), 2 g. p - $\text{MeC}_6\text{H}_4\text{NH}_2$ (I'), 0.9 g. p -azoxytoluene (J') and traces of $\text{MeC}_6\text{H}_4\text{OH}$ and 3,4-Me(OH) $\text{C}_6\text{H}_4\text{NH}_2$. 5 g. $\text{MeC}_6\text{H}_4\text{N}_2$, warmed with 1:3 H_2SO_4 for 2 hrs., gave 1 g. H', 0.4 g. I', and traces of $\text{MeC}_6\text{H}_4\text{OH}$. 22.5 cc. H_2SO_4 in 450 cc. H_2O , acting on 30 g. $\text{MeC}_6\text{H}_4\text{NHOH}$ for 14 hrs. at 18° gave 11-12 g. Me(HO) $\text{C}_6\text{H}_4\text{O}$ (K'), with Me(HO) $\text{C}_6\text{H}_4\text{NH}$ as an intermediate product. 1 vol. H_2SO_4 in 1.75 vols. H_2O acting for 11 hrs. at 50-70° on 22 g. $\text{MeC}_6\text{H}_4\text{N}_2$, gave 0.6 g. K', 5.4 g. I', 1 g. H', 0.1 g. $\text{MeC}_6\text{H}_4\text{OH}$. p - $\text{ONaC}_6\text{H}_4\text{Me}_2$ and H_2SO_4 , acting upon 4 g. $\text{MeC}_6\text{H}_4\text{NHOH}$ for 2 days, gave 5 g. $\text{H}_2\text{NC}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{MeNO}_2$; the same product was obtained from $\text{MeC}_6\text{H}_4\text{N}_2$. With PhOH and dil. H_2SO_4 , 4.95 g. $\text{MeC}_6\text{H}_4\text{NHOH}$ gave 3.4 g. $\text{MeC}_6\text{H}_4\text{NH}_2$, H_2O and $\text{MeC}_6\text{H}_4\text{OH}$ (L'), while 6 g. $\text{MeC}_6\text{H}_4\text{N}_2$ gave 4 g. L' and 0.3 g. H'. 1200 cc. MeOH and 30 cc. 100% H_2SO_4 , acting on 120 g. $\text{MeC}_6\text{H}_4\text{NHOH}$ for 24 hrs. at 10-20°, gave 6.2 g. Me(MeO) $\text{C}_6\text{H}_4\text{O}$ (M'), 3 g. p - $\text{MeC}_6\text{H}_4\text{NH}_2$, and 65 g. J'. 200 cc. MeOH and 100 cc. 100% H_2SO_4 , acting upon 73.5 g. $\text{MeC}_6\text{H}_4\text{N}_2$, gave 2.5 g. M' and 0.85 g. p -

$\text{MeC}_6\text{H}_4\text{NH}_2$. 1250 cc. EtOH and 35 g. 100% H_2SO_4 , reacting with 150 g. $\text{MeC}_6\text{H}_4\text{NHOH}$ for 15 hrs. at room temp., gave 10.9 g. $\text{Me}(\text{EtO})\text{:C}_6\text{H}_4\text{O}$ (N'), 11.9 g. p - $\text{MeC}_6\text{H}_4\text{NH}_2$ and 78 g. J' . 120 g. $\text{MeC}_6\text{H}_4\text{N}_2$, treated with 370 cc. EtOH and 170 cc. 100% H_2SO_4 at 8–17°, then for 10 hrs. at 10–20°, and finally for 40 hrs. at 25–30°, gave 4 g. N' and 2.2 g. p - $\text{H}_2\text{NC}_6\text{H}_4\text{Me}$. 10 g. 2,4-Me₂C₆H₄NHOH(O') with dil. H_2SO_4 (20 min. at 98°) gave 4 g. 1,4-(HO)₂C₆H₄Me, 2,5(P'), traces of 1,4-H₂N(HO)C₆H₄Me (I'), 1 g. 2,4-Me₂C₆H₄NH₂(R') and 0.4 g. (Me₂C₆H₄)₂N₂O. 60 g. 2,4-Me₂C₆H₄N₂(S') gave 0.4 g. P', 1.1 g. Q' and 1 g. R'. Dil. H_2SO_4 , acting on 35 g. O' for 8–10 days at 23–25°, gave 22 g. $\text{Me}(\text{OH})\text{:C}_6\text{H}_4\text{Me}\text{O}(\text{T}')$, 6 g. R', 2.5 g. (Me₂C₆H₄)₂N₂O, traces of Q', while 10 g. S' gave 1.2 g. T', 0.7 g. R', and 0.3 g. P'. EtOH and concd. H_2SO_4 with 100 g. O', gave 30 g. $\text{Me}(\text{EtO})\text{:C}_6\text{H}_4\text{Me}\text{O}(\text{U}')$, 7 g. (EtO)₂C₆H₄Me (V'), 0.15 g. Me₂C₆H₄(HO)(OEt), 0.2 g. Me₂C₆H₄OH, etc. 200 g. Me₂C₆H₄N₂ treated with 2 vols. EtOH and 1 vol. H_2SO_4 for 50–60 hrs. at room temp., gave 14.9 g. U', 11.2 g. T', 5 g. Me₂C₆H₄OH, 3.2 g. P', 8 g. R', etc. 110 g. Me₂C₆H₄N₂ treated with MeOH and concd. H_2SO_4 for 28 hrs., gave 11 g. $\text{Me}(\text{MeO})\text{:C}_6\text{H}_4\text{Me}\text{NH}$, 27 g. $\text{Me}(\text{MeO})\text{:C}_6\text{H}_4\text{Me}\text{O}$, 1.4 g. T', 3.2 g. R', etc. EtOH and H_2SO_4 gave with 140 g. Me₂C₆H₄N₂, 9.2 g. $\text{Me}(\text{EtO})\text{:C}_6\text{H}_4\text{Me}\text{NH}$, 14 g. U', 1.5 g. T', 0.05 g. P', 0.35 g. V', 3.1 g. Me₂C₆H₄NH₂, etc. Concd. HCl, acting on 85 g. Me₂C₆H₄NHOH for 2 weeks at 0°, gave 32 g. 2,4,6-Me₂C₆H₄NH₂ (W'), 29 g. 2,4,5-Me₂C₆H₄NH₂(X'), etc. 12 g. Me₂C₆H₄N₂ gave 4.1 g. W' and 6.4 g. X'. Satd. HBr, reacting with 80 g. Me₂C₆H₄NHOH for 7 weeks, gave 45 g. 2,4,6-Me₂BrC₆H₄NH₂(Y'), 0.7 g. 2,4,5-Me₂BrC₆H₄NH₂(Z'), 7.5 g. R', etc. 20 g. Me₂C₆H₄N₂ treated with satd. HBr for 2 days, gave 17.2 g. Y', traces of Z', 1.2 g. R', etc.

C. J. WEST

Behavior of arylhydroxylamines towards halogen acids. EUGEN BAMBERGER. Zürich. *Ann.* 424, 297–321 (1921); cf. preceding abstr.—Dil. HCl, reacting with 2 g. PhNHOH(A), gave 1.6 g. p -ClC₆H₄NH₂(B), very little p -NH₂C₆H₄OH(C), and 0.2 g. Ph₂N₂O(D). 60 g. A with HCl satd. at 0°, gave 37 g. B, 15 g. o -ClC₆H₄NH₂, 0.2 g. 2,4-Cl₂C₆H₄NH₂, 0.2 g. D, traces of C, and of *sym*-ClC₆H₄NH₂. Dil. HBr and 3 g. A gave 38% pure p -BrC₆H₄NH₂(E). HBr satd. at 0°, reacting with 60 g. A, gave 22 g. pure E, 5.3 g. o -BrC₆H₄NH₂, 2.5 g. 2,4-Br₂C₆H₄NH₂ and 4 g. PhNH₂. Dil. H₁ and 3 g. A gave 1.2 g. pure D, 0.6 g. PhNH₂, while concd. H₁ and 5 g. A gave 2 g. PhNH₂, but no D. Concd. aq. HF and 4 g. A gave 0.1 g. D, and 4.2 g. of a greenish amorphous product, insol. in dil. H₁. 30 g. 2-MeC₆H₄NHOH(F) and concd. HCl gave 13 g. 2,4-MeClC₆H₄NH₂, 1 g. 2,5-MeClC₆H₄NH₂, about 0.3 g. 2,6-MeClC₆H₄NH₂; HBr, reacting with 26 g. F, gave 10 g. 2,4-MeBrC₆H₄NH₂, 4.3 g. 2,4,6-MeBrC₆H₄NH₂, 4.7 g. of a mixt. of 2-MeC₆H₄NH₂ and 2,4-MeBrC₆H₄NH₂, 3 g. 3-MeC₆H₄NHOH(G) and dil. HCl (1:4) gave 0.6 g. 3,4-MeClC₆H₄NH₂(H), 0.8 g. 3,4-Me(HO)C₆H₄NH₂(I), while 410 g. G and concd. HCl gave 250 g. pure H, 9.9 g. 2,3-ClMeC₆H₄NH₂ and a little 3,6-MeClC₆H₄NH₂. Dil. HBr and 3 g. G gave 0.8 g. 3,4-MeBrC₆H₄NH₂(J), 0.3 g. I, while concd. HBr with 4.5 g. G gave 2.5 g. J. Dil. HCl and p -MeC₆H₄NHOH (see preceding abstr.). Concd. HCl and 85 g. 2,4-Me₂C₆H₄NHOH(K) gave 32 g. 2,4,6-Me₂ClC₆H₄NH₂, 29 g. 2,4,5-Me₂ClC₆H₄NH₂ and 7 g. azoxytoluene. Satd. HBr and 80 g. K gave 0.07 g. 2,4,5-Me₂BrC₆H₄NH₂, 45 g. 2,4,6-Me₂BrC₆H₄NH₂, 7.5 g. 2,4-Me₂C₆H₄NH₂, 8.2 g. azoxytoluene. 13 g. 3,6-Me₂C₆H₄NHOH(L) and satd. HCl gave 9.5 g. 2,6,4-Me₂ClC₆H₄NH₂; satd. HBr and 11.2 g. L gave 11–12 g. 3,6,4-Me₂BrC₆H₄NH₂, 1–1.5 g. 3,6,1,4-Me₂BrC₆H₄NH₂, about 0.5 g. 3,6-Me₂C₆H₄NH₂, 5.5 g. p -chlorophenylhydroxylamine (M), m. 182°, and dil. HCl gave 2.4 g. 2,4-Cl₂C₆H₄NH₂(N), 0.7 g. p -ClC₆H₄NH₂(O) and 1.5 g. (ClC₆H₄)₂N₂O. Fuming HCl and 7 g. M gave 4 g. N, 0.8 g. O, and 0.45 g. 2,4,6-Cl₂C₆H₄NH₂(P). HCl, acting upon a C₆H₆ soin. of 3.5 g. M, gave 1.25 g. N, 0.5 g. O and very little P. Satd. HBr and 12 g. M gave 7 g. 2,4-BrClC₆H₄NH₂, 3.4 g. 2,6,4-BrClC₆H₄NH₂, and 2 g. O. Dil. HCl

and 3 g. $\text{BrC}_6\text{H}_4\text{NHOH}$ (Q) gave 1.3 g. 2,4-CI₂BrC₆H₄NH₂ (R), 0.3 g. $\text{BrC}_6\text{H}_4\text{NH}$, (S), and 0.7 (BrC₆H₄)₂N₂O. HCl satd. at 0° and 11 g. Q gave 5.7 g. R, 1.9 g. 2,6,4-CI₂BrC₆H₄NH₂ and 1.7 g. S. Dil. HBr and 6 g. Q gave 1.9 g. 2,4-Br₂C₆H₄NH₂(T), 1 g. ρ -BrC₆H₄NH₂(U), and 2.3 g. (BrC₆H₄)₂N₂O. HBr satd. at 0° and 11 g. Q gave 5.7 g. T, 2.8 g. U, and 2.5 g. 2,4,6-Br₃C₆H₄NH₂. 15 g. *m*-BrC₆H₄NHOH and dil. HCl gave 3,4-BrC₆H₄NH₂ and a little 3,6-BrC₆H₄NH₂, while dil. HBr gave about 50% yield of (*m*-BrC₆H₄)₂N₂O. From these results it is seen that if the ρ - and *o*-H atoms of the arylhydroxylamines are not replaced, ρ -haloanilines are formed and often simultaneously the *o*-derivs. When the *p*-H atom is substituted, then *o*- and sometimes *m*-derivs. are formed. Another reaction also takes place, resulting in the formation of the aniline and the dihalogen deriv. The formation of the trisubstituted deriv. is probably the result of the action of the concd. acid upon the haloanilines formed as above. The hypothesis proposed for the reaction is: PhNHOH → PhNHCl → H(Cl):C₆H₄:NH → CIC₆H₄NH₂.

C. J. WEST

Preparation of the mixed secondary and tertiary phenolic amines. A. MAILHE AND F. DE GODON. *Compt. rend.* 172, 1417-9(1921).—In *C. A.* 12, 1383, 1550, the catalytic production of the above was illustrated. This paper is an extension of the method to the methylation and ethylation of PhNH₂, MeC₆H₄NH₂, Me₂C₆H₃NH₂, α - and β -C₁₀H₈NH₂ and Ph₂NH. In each case the amine was dissolved in the proper alc. and the vapor of this mixt. was passed over an alumina catalyst heated to 350–380°. Little C₆H₄ was generated as indicated by the small amt. of uncondensable gas set free and in every case ether was recovered in rectifying the condensate. PhNH₂ and 2 vols. of 95% EtOH were first tried. The product formed 2 layers. The lower consisted of water, EtOH and Et₂O, the upper gave a yellow liquid on rectification. The b. p. rose after removal of the Et₂O from 195° to 204° and was a mixt. of PhNH₂, PhNHET and PhNET₂. When samples form no solid on testing with dil. H₂SO₄ we have all the PhNHET and PhNET₂. A nitrosation study showed this to be mainly PhNHET. The fraction between 195–284° is mixed with more EtOH and re-treated with the catalyst to complete the ethylation. This requires 3–4 treatments. With MeOH one treatment is sufficient. MeC₆H₄NH₂ (all three) were all ethylated completely by 2 exposures to the catalyst. The xylidines are easily ethylated. *m*-Xylidine with 2 vols. of EtOH gave a mixt., b. 216–23°, of Me₂C₆H₃NHET and Me₂C₆H₃NET. The *o*- and ρ -xylidines, mixed with 2 vols. EtOH and treated twice with the catalyst, gave a mixt. containing no unchanged xylidine. α - and β -C₁₀H₈NH₂ being sparingly sol. require a large excess of alc. but on a single passage over the catalyst are completely changed into a mixt. of ethylated amines. The conversion of Ph₂NH into Ph₂NMe and Ph₂NET by MeOH and EtOH, resp., produce products b. 282° and 287–3° each. The conversion is complete.

R. E. SABIN

New method for the preparation of α -acylphenylhydrazines. WALLACE FRANK SHORT. Univ. College, Auckland, N. Z. *J. Chem. Soc.* 119, 1445–8(1921).—Acylchloroaminobenzenes react with NH₃ with quant. evolution of 1 mol. N₂ from 3 mols. chloroamine. By treating a cold C₆H₆ soln. of the chloroanilides with a suspension of finely powdered NaNH₂ in C₆H₆, excellent yields of the α -acylhydrazines may be obtained. The NaNH₂ must be dry and free of NaOH. Thus, PhNAcNH₂ may be prepd. by treating 12 g. NCIPhAc in dry C₆H₆ with a C₆H₆ suspension of 2.6 g. NaNH₂, the reaction being carried out in a stream of H and just above the f. p. of the mixt. After 0.5 hr., the mixt. is warmed on the H₂O bath for 10 min. Yield, 80%. MeC₆H₄NAcNH₂ and PhNBzNH₂ were prepd. in the same way. By the action of PhNAcNa upon NCIPhAc, a 60% yield of (PhNAc)₂ was obtained.

C. J. WEST

Aromatic arsenic compounds. IX. Diazoamino compounds of arsanilic acid and its derivatives. WALTER A. JACOBS AND MICHAEL HEIDELBERGER. *J. Am. Chem.*

Soc. 43, 1633-45(1921); cf. C. A. 14, 280.—In carrying out the plan outlined in C. A. 13, 2668, for the synthesis of aromatic As compds. for chemotherapeutic study, diazoamino and azo derivs. of arsanilic acid (A) were the first prep'd. but because of disadvantages which seemed inherent in these compds., such as the general instability of the diazoamino derivs. and certain harmful toxic effects induced by both the diazoamino and diazo groups, their study was discontinued. J. and H., however, in the present papers give a brief description of their chem. study of these compds. Secondary aliphatic amines and the simpler primary aromatic amines in general couple readily with diazotized A, the reaction being kept neutral or acid with a weak acid such as AcOH and the product being isolated either as the salt or as the acid, depending upon manipulative convenience. In certain cases, however, it was found preferable to diazotize the NH₂ compd. first and then add A as the coupler. With *p*-HNC₆H₄OCH₃CO₂H and its homologs it was found that either the reaction did not proceed entirely in the desired direction or that the diazoamino compds. could be isolated only with difficulty, while the esters couple smoothly and the resulting diazoanilino esters can be saponified to the free acids with relative ease. The diazoamino compds. from the sec. aliphatic amines and most of the aromatic NH₂ compds. form both cryst. acids and Na salts, the former having definite decompr. points and being as a rule difficultly sol. in the usual solvents, while the salts yield more or less yellow aq. solns. The acids are unstable in acid soln., readily dissociating into the component NH₂ and diazo compds. and evolving N on warming. Practically all the Na salts are readily sol. in H₂O and at once give ppts. with the heavy-metal ions. In each case the conditions best suited for the prep'n. and isolation of the particular compd. had to be worked out carefully and it was found essential to work as rapidly as possible throughout and at low temps. The following diazobenzene-[4-arsonic acid]-amines were prep'd.: *Dimethylamine*, H₂OAsC₆H₄N:NMe₂, orange spears from alc., intumesc 182°; *sodium salt*, salmon-colored platelets with 3.5 H₂O from 85% alc. *Diethylamine*, flat cream-colored needles with 1 H₂O from 50% EtOH-H₂O, soften and darken (anhydrous) above 120°, decomp. about 195-200°; *sodium salt*, rosets of somewhat deliquescent cream-colored needles from 85% alc. *Piperidine*, pale drab spherules and rosets of narrow microplatelets, m. 162-3° (effervescence); *sodium salt*, minute drab platelets with 3.5 H₂O from 85% alc. *Bisdiazobenzene-[4-arsonic acid]-pentamethyleneetriamine*, C₁₁H₂O₄N₂As₂, narrow microplatelets, puffs up 210-2°, obtained from diazotized A and hexamethylenetetramine, with cleavage of HCHO, as the *sodium salt*, platelets with 6 H₂O, sol. in about 20 parts H₂O at room temp. *Diazobenzene-[4-arsonic acid]-aniline*, yellow microneedles, m. and then decomps. 112-3°; *sodium salt*, minute orange platelets and flat needles with 4 H₂O from 85% alc. *Methylaniline*, orange-brown aggregates of minute radiating needles from very dil. aq. NH₄OH and alc. + AcOH, effervesces 160-2°, sol. in dil. acids with orange-red color; *sodium salt*, orange platelets with 5.5 H₂O. *p-Toluidine*, thin, pale yellow microneedles from 50% alc., intumesc 180-2°; *sodium salt*, yellow leaflets with 6 H₂O from H₂O containing a little Na₂CO₃. *4'-Chloroaniline*, hexagonal tablets, intumesc 177°; *sodium salt*, platelets, with 2 H₂O from 50% alc. *o-Anisidine*, flat microneedles with 2.5 H₂O from 50% alc., sinters (anhydrous), then darkens and finally intumesces 95-9°; *sodium salt*, brown rectangular platelets with 5 H₂O from 85% alc. *p-Anisidine*, pale brown, microneedles with 0.5 H₂O from 33% alc., begins to decomps. about 110°, intumesces (anhydrous) 116-8°; *sodium salt*, pale brown leaflets with 5 H₂O from 50% alc. *4'-Aminocetanilide*, long, drab hexagonal microtablets with 1 H₂O from 50% alc., decomps. (anhydrous) 165-70°; *sodium salt*, tan microleaflets with 5 H₂O from 50% alc. *4'-Aminophenyl benzoate* (12 g. from 6.4 g. *p*-HNC₆H₄O₂Z in 60 cc. N HCl diazotized at 10° with 2.2 g. NaNO₂ and coupled with 6.6 g. A in 30 cc. N NaOH), thin, yellow

microleaflets from MeOH-H₂O, decomp. 155-8°. *4'-Aminophenol*, obtained as the *sodium salt*, yellow microneedles with 4 H₂O from 85% alc. *4'-Aminacetophenone*, bright yellow microneedles, intumesces 177-8°; *sodium salt*, minute, brownish yellow, flat needles with 6 H₂O from 85% alc. *2'-Aminobenzoic acid*, thin, yellow microneedles, intumesces 160°; *monosodium salt*, flat, yellow microneedles with 4.5 H₂O; *disodium salt*, long, flat, yellow needles with 8 H₂O from 85% alc. *3'-Aminobenzoic acid*, buff microcryst. rosets from 50% alc., intumesces 141°; *monosodium salt*, cream-colored crystals; *disodium salt*, long, thin, pale yellow microneedles with 6.5 H₂O from 70% alc. *4'-Aminobenzoic acid*, flat microneedles; *monosodium salt*, microneedles from 50% alc. *3'-Amino-6'-methoxybenzoic acid*, yellow microneedles with 1.5 H₂O from 50% alc., decomp. (anhydrous) 140°; *disodium salt*, pale brownish yellow bygroscopic needles from 70% alc., obtained by sapon. of the *dimethyl ester*, narrow, buff platelets with 3 H₂O from EtOH-H₂O, m. 90-5° (gas evolution). *3'-Aminoanisic acid*, yellow microneedles with 1.5 H₂O from 50% alc., intumesces (anhydrous) 150-5°; *disodium salt*, fine, yellow needles with 10 H₂O; *dimethyl ester*, yellow needles with 2.5 H₂O from 50% alc., decomp. about 150°. *6-Aminopiperonic acid* and the *sodium salt* were not obtained analytically pure; the *monomethyl ester*, short, flat, almost colorless needles, does not decomp. 280°. *4'-Aminocinnamic acid*, fine yellow microneedles, decomp. 155-60°; *monosodium salt*, bright yellow microneedles with 6 H₂O from 70% alc. *4'-Aminocinnamic acid*, yellow microneedles with 0.5 H₂O from 50% alc., decomp. (anhydrous) 155-60°; *disodium salt*, yellow microneedles with 6 H₂O from 70% alc. *4'-Aminophenylarsonic acid*, pale yellow microneedles from 95% alc., intumesces 154°; *monosodium salt*, thin yellow platelets with 2.5 H₂O from 50% alc.; *disodium salt*, delicate, yellow needles with 7 H₂O from 50% alc. *Phenylglycine*, could not be obtained cryst.; *sodium salt*, flat, brown-yellow microneedles with 2 H₂O from 50% alc. *p-Tolylglycine*, flat, pale, terra cotta-colored microneedles from 50% alc., intumesces 148-9°; *sodium salt*, tan microneedles with 1.5 H₂O. *Benzylglycine*, almost colorless microneedles and prisms from EtOH-H₂O, intumesces 155-60°. *4'-Methoxyphenylglycine ethyl ester*, obtained as the *sodium salt*, yellow-brown leaflets and flat needles with 4 H₂O from 85% alc.; *glycine sodium salt*, yellow microplatelets with 2 H₂O. *4'-Ethoxypyrenylglycine ethyl ester*, almost colorless microrhombohedrons from 25% alc.; *sodium salt*, cream-colored leaflets with 2.5 H₂O from 70% alc.; *glycine sodium salt*, thin, yellow microneedles with 2 H₂O. *4'-Aminophenoxyacetic acid*, microcrystals, m. 132° (*disodium salt*, brown needles with 6.5 H₂O from 85% alc., gradually darkens and decomp. on standing); *ethyl ester*, minute, salmon-colored leaflets from 50% alc., m. 132-3° (decompn.) (*sodium salt*, brownish microneedles with 5 H₂O from 85% alc.). *p-Aminophenoxyacetamide*, cream-colored microneedles and hairs from 50% alc., m. 162° (effervescence); *sodium salt*, delicate drab needles with 8 H₂O from 50% alc. *p-Aminophenoxyacetmethylamine*, minute, flat, cream-colored needles with 1 H₂O from 50% alc., m. 170° (decompn.); *sodium salt*, hair-like needles with 4 H₂O. *4'-Methylaminophenoxyacetic acid*, greenish yellow microspindles, m. 155-60°. *3'-Methyl-4'-aminophenoxyacetic acid*, obtained as the *disodium salt*, light brown hydrated plates, from the *methyl ester*, minute needles, m. 105-7° (decompn.) (*sodium salt*, reddish brown microneedles). *2'-Methyl-4'-aminophenoxyacetic acid*, likewise obtained as the *disodium salt*, long, flat, pinkish yellow microneedles with 4.5 H₂O, slowly decomp., on exposure, from the *methyl ester*, purple-brown microleaflets from 50% alc., decomp. 143-4°. *2',5'-Dimethyl-4'-aminophenoxyacetic acid* and the *disodium salt*, pale yellow needles, were not obtained analytically pure; the *methyl ester*, gray-yellow, short, flat, pointed microneedles with 1.5 H₂O, decomp. 120°. *2'-Methyl-5'-isopropyl-4'-aminophenoxyacetic acid*, obtained as the *disodium salt*, minute, flat, pale brown needles with 9.5 H₂O from H₂O-EtOH; *methyl ester*, microneedles, decomp. 145°. *3'-Methyl-*

6'-isopropyl-4'-aminophenoxyacetic acid; disodium salt, yellow microleaflets with 4 H₂O from H₂O-EtOH; *methyl ester*, yellow microleaflets with 1.5 H₂O from 50% alc., intumesces about 130° on rapid heating, turns orange above 120° on slow heating, then gradually darkens but does not m. 275°. *2'-Bromo-4'-aminophenoxyacetic acid*, delicate, pale yellow microneedles with 3 H₂O, decomp. (anhydrous) about 120°; *disodium salt*, flat, pale brownish yellow needles with 4 H₂O; *methyl ester*, long, curved cream-colored microneedles, decomp. 154–5°. *2-Methyl-4-amino-6-bromophenoxyacetic acid*, grayish microcryst. aggregates from 50% alc., decomp. about 155°; *disodium salt*, indefinitely cryst., sol. in H₂O with deep orange color; *methyl ester*, delicate pinkish microneedles, intumesces 188°. *4'-Amino-6'-acetylphenoxyacetic acid* was not obtained pure; *disodium salt*, pale brown microleaflets with 5 H₂O from H₂O-EtOH; *methyl ester*, hair-like needles, effervesces and reddens about 155°. *Diazo-2-methylbenzene-[4-arsenic acid]-p-aminophenoxyacetic acid*, obtained as the *disodium salt*, minute, brownish leaflets with 6.5 H₂O; *methyl ester*, minute, flat needles, decomp. 130–2° (*sodium salt*, drab microneedles). *Diazo-2-bromobenzene-[4-arsenic acid]-p-aminophenoxyacetic acid*, drab microcrystals from 50% alc., intumesces about 130°; *disodium salt*, minute drab crystals with 4 H₂O; *methyl ester*, brownish microneedles, intumesces 123–5° (*sodium salt*, pinkish hairlike microneedles). X. *Azo dyes derived from arsanilic acid*. *Ibid* 1646–54. In the course of the preceding work it was found that certain classes of aromatic NH₃ compds. yield aminoazo dyes at once when coupled with diazotized arsanilic acid (A) or give diazoamino compds. which rapidly rearrange into the dyes. *o-MeNH₂C₆H₄CO₂H* added to the neutralized diazo soln. rapidly gives the diazoamino compd. which slowly rearranges into the dye on standing or rapidly on acidification with AcOH; the *N*-Et and *N*-isooamyl compds. behave similarly. Under the usual conditions of coupling in neutral or slightly acid soln. *m-H₃NC₆H₄OCH₃CO₂H* (B) at once gives a dye in which it is assumed that the azo group has entered the *p*-position to the NH₃ group. Azo derivs. were also obtained from 2 groups of substitution products of *m*-anisidine and B in one of which the *p*-position to the NH₃ group is free and in the other of which this position is occupied by a substituent; in these two classes of compds. the azo group probably enters the *p*- and *o*-positions, resp., to the NH₃ group. Finally, the *o*-Me, *o*-MeO and *o*-EtO derivs. of phenylglycine (C) at once form dyes under the conditions under which the unsubstituted C gives principally the diazoamino compd. (preceding abstr.). In most cases the reaction between the diazotized A and the coupler proceeded smoothly with very little gas evolution but the isolation and purification of the resulting dye often presented considerable difficulty and much experimentation was necessary to discover the best conditions of coupling and whether the dye could best be isolated as the free acid or the mono- or di-Na salt. The mono-Na salts are generally very sparingly sol. in H₂O, the di-Na salts readily sol.; even very dil. solns. of the latter immediately give amorphous ppts. with salts of the heavier metals. The following compds. are described. *Benzene-4'-arsenic acids*: *1-Amino-2-methoxynaphthalene-4-azo*, narrow, bluish black microplatelets with 1.5 H₂O from 50% alc., does not m. 285°, sol. in concd. H₂SO₄ with deep purple and in dil. NaOH with deep cherry-red color; *1-amino-4-methoxy-naphthalene-2-azo*, dark brown microcryst. aggregates with 1.5 H₂O, sinters, darkens, softens about 195°, intumesces about 225°, sol. in concd. H₂SO₄ with purplish red color changing to brown-red and again to purplish on diln., sol. in dil. NaOH with deep cherry-red color; *4-methylamino-5-carboxyphenylazo*, brick-red, thin microneedles and plates from 50% alc., does not m. 280°, sol. in concd. H₂SO₄ with deep orange, in hot 10% HCl with red color (the hydrochloride sepg. on cooling in narrow purplish red plates with steel-blue reflex), gives in dil. HCl with NaNO₂ a ppt. (presumably the *nitroso compound*) of pale salmon-colored microneedles, forms a *monosodium salt*,

short, brownish yellow microneedles with 2.5 H₂O, and a *disodium salt*, flat, red microneedles with 8.5 H₂O from 70% alc.; *4-ethylamino-5-carboxyphenylazo*, deep orange rectangular platelets from 85% alc., does not m. 275°; *4-isooxylamino-5-carboxyphenylazo*, orange-red striated platelets from AcOH, does not m. 275°, sol. in concd. H₂SO₄ with deep red-orange, in concd. HCl with deep red color (*hydrochloride*, dark microneedles; *sodium salt*, orange microleaflets with 2 H₂O); *4-amino-2,3-dimethoxy-5-carboxyphenylazo*, long, narrow, orange-red platelets with 2 H₂O from 85% alc., is deeper red when anhydrous, does not m. 275°, sol. in concd. H₂SO₄ with deep orange, in boiling 10% HCl with dark red color (*hydrochloride*, brown platelets and flat needles; *sodium salt*, flat, brown-orange microneedles with 2.5 H₂O); *2-amino-4,5-dimethoxy-3-carboxyphenylazo*, brown leaflets and microcryst. aggregates with about 1.5 H₂O from 50% alc., turns darker brown on dehydration, decomp. somewhat on heating but does not m. 290°, sol. in dil. acids with red color changing to orange only on high diln., sol. in concd. H₂SO₄ with intense red color, only partially sol. in concd. HCl (*hydrochloride*, dark orange-red microcryst. spherules; *sodium salt*, orange-red microcrystals with 1.5 H₂O, becoming chocolate-brown when air-dried, sol. in alkalies with orange color). *4-[Phenyl-(4'-arsonic acid)-azo]phenylglycine* (5.3 g. from a diazotized soin. of 4.4 g. A added to 3.1 g. C in 40 cc. N HCl dild. to 100 cc. with 0.5 N HCl), orange-red lenticular platelets with 0.5 H₂O from 50% alc., m. 170-5° (decompn.), sol. in dil. alkalies with reddish orange, in concd. H₂SO₄ or 1:1 HCl with deep red color (*hydrochloride*, red microneedles with purplish luster); *2-methyl derivative*, red-brown needles, leaflets and rhombic platelets with 1 H₂O, intumesces 157°, sol. in concd. H₂SO₄ with deep red color (*hydrochloride*, minute, dark brown platelets with purple luster); *2-methoxy derivative*, steel-blue platelets with 1.5 H₂O, m. about 160° (effervescence), intumesces (anhydrous) 167°, sol. in concd. H₂SO₄ with deep purple, in 1:1 HCl with deep red, in dil. carbonates or alkalies with orange color (*sodium salt*, thin, pearly, orange-red platelets with about 2.5 H₂O, sol. in H₂O with deep red color changing to brown and sepr. in microcryst. spherules of what is apparently another hydrate; addition of NaOAc or NaOH produces a clear deep orange soin.); *2-ethoxy derivative*, flat, purplish brown microneedles, decomp. 245-50°, sol. in H₂SO₄ with deep red color, appearing purple in thin layers (*sodium salt*, orange-brown platelets with 2.5 H₂O from 50% alc., sol. in H₂O with brown-red color). *α'-[Phenyl-(4'-arsonic acid)azo]-α-naphthylglycine*, crystals with 0.5 H₂O from 25% alc., m. about 275° (decompn.), sol. in H₂SO₄ with deep red color in H₂SO₄, appearing purple in thin layers; *disodium salt*, crystals from 85% alc. sol. in H₂O with purple color. *4-[Phenyl-(4'-arsonic acid)-azo]phenylaminomethylsulfonic acid*, H₂OAsC₆H₄N:NC₄H₄NHCH₂SO₃H, flat, red needles with 2 H₂O from 25% alc., sol. in boiling H₂O with red color, turns bright red when heated rapidly to 185°, m. partially 187-9°, sol. in H₂SO₄ with a deep orange color quickly fading to yellow (*disodium salt*, delicate orange needles with 4.5 H₂O from 50% alc.); *2-methoxy derivative*, flat, violet needles with 1.5 H₂O from 50% alc., reddens and softens (anhydrous) above 155°, m. 158-60° (slow gas evolution), sol. in H₂SO₄ with deep purple color changing to deep red on standing (*disodium salt*, orange-red microneedles with 3 H₂O, sol. in H₂O with deep orange-red color). *3-Amino-6-[phenyl-(4'-arsonic acid)azo]phenoxyacetic acid*, red needles with 1.5 H₂O, blackens (anhydrous) but does not m. 285°, sol. in concd. H₂SO₄ with orange-red, in dil. alkalies with orange, in 1:1 HCl with orange-red color (*sodium salt*, orange microcrystals; *hydrochlorides*, orange-brown microcrystals); *4-methyl homolog*, flat, dark red needles with 1 H₂O, intumesces 242-3° when heated rapidly to 240°, sol. in concd. H₂SO₄ and dil. alkalies with orange color (*sodium salt*, red crystals; *hydrochloride*, orange-red microcrystals). *2-Methyl-5-amino-4-[phenyl-(4'-arsonic acid)azo]phenoxyacetic acid*, flat, purplish brown needles with 2 H₂O from 33% alc., intumesces 187-8°, sol. in concd. H₂SO₄ with deep orange,

partially in concd. HCl with red color (*hydrochloride*, dull red microcrystals); *3-amino-6-methoxy compound*, flat, bronze needles and platelets with 4.5 H₂O from 50% alc., swells (hydrated) 175–85°, intumesces (anhydrous) 208–13°, sol. in dil. alkalies or carbonates with orange-red, in concd. H₂SO₄ with bright red, in 1:1 HCl with deep purplish red color (*hydrochloride*, dark brown microplatelets). *4-Amino-6-methoxy-3-[phenyl-(4'-arsonic acid)]azophenoxyacetic acid*, minute maroon platelets with 2 H₂O from 50% alc., does not m. 280°, sol. in H₂SO₄ with bright red color (*sodium salt*, chocolate microneedles with 6.5 H₂O from dil. NaOAc; *hydrochloride* flat, dark red needles. *4-Amino-5-[phenyl-(4'-arsonic acid)]azo-1,2-bisphenoxyacetic acid*, dark purplish microcrystals with 3 H₂O from 50% alc., softens and sinters (anhydrous) on heating but does not m. 280°, sol. in H₂SO₄ with orange-red color (*sodium salt*, dark purplish brown microcryst. spherules with 4.5 H₂O, sol. in alkalies or carbonates with orange-red color). *α-Amino-β-[phenyl-(4'-arsonic acid)]azo-α'-naphthoxycetic acid*, flat dark red needles with golden luster from 50% alc., decomp. about 285°, sol. in concd. H₂SO₄ with deep purplish red color; *disodium salt*, dark brown felted microneedles with 9 H₂O from 50% alc., sol. in H₂O with dark purplish red color. *α-Amino-α'-[phenyl-(4'-arsonic acid)]azo-β-naphthoxycetic acid*, red-brown microcrystals with 1 H₂O from 50% alc., does not m. 285°; *disodium salt*, almost black microhairs with 8.5 H₂O from 50% alc., sol. in H₂O with deep red color. *2-Hydroxy-5-[phenyl-(4'-arsonic acid)]azo-phenoxyacetic acid*, brown microplatelets with 0.5 H₂O from aq. soln., does not m. 280°, sol. in dil. NaOH with bright orange, in concd. H₂SO₄ with deep red-orange color; *sodium salt*, yellow, indefinitely cryst. microglobules from 50% alc. C. A. R.

Some additive compounds derived from arsines. GEORGE JOSEPH BURROWS AND EUSTACE EBENEZER TURNER. Univ. Sydney. *J. Chem. Soc.* 119, 1448–50 (1921); cf. *C. A.* 15, 510.—The following additive compounds were prep'd.: PhMe₂As.PI₄, from 1 mol. of each of the components in CS₂, orange prisms, m. 140°. PhMe₂As.ASI₁, from boiling CHCl₃ as orange-red leaflets, m. 153°. PhMe₂As.SHI₁, from C₆H₆ orange prisms, m. 165°. PhMe₂As.BII₁, vermillion prisms from alc., m. 108–200°. 2 PhMe₂As.SNI₁, chocolate-colored leaflets from CS₂, m. 140–5°. 2 PhMe₂As.CDI₁, from the components in aq. soln., m. 194°. PhMe₂EtAs.HgI₂, pale yellow prisms, m. 135°, from the components in dil. AcMe. PhMe₂EtAs.PbI₂, pale yellow prisms, m. 203°. Tertiary amines combine with ASI₁ and with iodoarsines to give yellow solids which are readily hydrolyzed to the hydroiodide of the base in question. C. J. WEST

Derivatives of sulfur in commercial salvarsan. II. HAROLD KING. Nat. Inst. Med. Research, Hampstead. *J. Chem. Soc.* 119, 1415–20 (1921); cf. *C. A.* 15, 3085.—This part contains proof of the constitution of 3-amino-4-hydroxy-5-sulfophenylarsonic acid (A). 2,4-HO₂S(O₂N)C₆H₃OH, prep'd. by adding 30 g. *p*-O₂NC₆H₄OH to 80 g. H₂SO₄ (16% SO₄) at –10° and keeping at 0° for 24 hrs., and isolating as the Ca salt, was reduced with Sn and HCl to the NH₂ deriv. (Ger. pat. 113,337), which was then diazotized in HCl and treated with Cu powder; the acid was isolated as the ammonium salt, C₆H₃O₂N₂S, long, glistening, delicate golden leaflets, readily sol. in hot H₂O and giving a wine-red color with FeCl₃. *Lewd salt*, orange-yellow prisms with wedge-shaped ends, or hexagonal plates. *6-Nitrophenol-o-sulfonic acid*, from the Pb salt by decomprn. with H₂S, delicate, pale yellow needles, very sol. in H₂O, is not extd. by Et₂O and is not pptd. by addition of concd. HCl to the solid NH₄ salt. Reduction of the NH₂ salt by Sn and HCl gave *6-aminophenol-o-sulfonic acid*, identical with the acid obtained by hydrolysis (Karrer's method) of [3,4,5-H₂N(HO)(HO₂S)C₆H₃As=]_n crystals with 0.5 H₂O; *barium salt*, rosets of glistening hexagonal leaflets. NaNO₂ and HCl gave an orange-red soln. which gave a blue dye with β-C₁₂H₂₁OH·FeCl₃ gives an intense cherry-red color. On nitration *4-nitro-6-aminophenol-o-sulfonic acid* is formed, which seps. as a stable monohydrate in columns or stout prisms,

losing H_2O at 140° , as a dimorphous dihydrate, long, glistening needles, which slowly pass into soln. with deposition of a 2nd dihydrate, flattened, serrated needles, or of the stable monohydrate. It decomp. violently at 235° ; ammonium salt, diamond-shaped leaflets; diazotized, the acid gives an insol. red dye with $\beta\text{-C}_10\text{H}_7\text{OH}$. The isomeric 6-nitro-4-amino acid is not changed at 290° ; the ammonium salt forms needles as does the barium salt, the salts being more sol. than those of the isomeric acid. Both acids upon reduction give 4,6-diaminophenyl-o-sulfonic acid, the hydrochloride of which seps. in diamond-shaped leaflets from H_2O , while the base seps. as microplates or leaflets. The barium salt forms nodules or warts. $FeCl_3$ gives a deep red rapidly darkening to purple. Diazotized, $\beta\text{-C}_10\text{H}_7\text{OH}$ gives a purple-blue dye. A, on reduction, gave the corresponding arsenious acid (not the sulfinoarsinic acid of the first communication).

C. J. Wurst

Action of organomagnesium compounds on arylsulfonyl chlorides. E. WEDGKIND AND D. SCHENK. Forstl. Hochschule in Hann.-Münden. *Ber.* **54B**, 1604-12 (1921).—The course of the reaction between Grignard reagents and sulfonyl chlorides differs entirely from that with carboxylic chlorides and depends, moreover, on the nature of the components. Thus, when 33 g. Mg and 148 g. Et_2Br in 300 cc. Et_2O are slowly treated in ice with 65 g. $p\text{-MeC}_6H_4SO_2Cl$ in 250 cc. Et_2O , allowed to stand about 12 hrs. at room temp. with frequent shaking, decompd. with ice and very dil. H_2SO_4 and washed with H_2O , the aq. soln. on evapn. and extn. with alc. yields $(p\text{-MeC}_6H_4SO_2)_2Mg$ and the Et_2O soln. on evapn. and distn. with steam gives 15 g. of the volatile $p\text{-MeC}_6H_4SEt$, $b_{10} 117-9^\circ$, and a small amt. of the non-volatile $(p\text{-MeC}_6H_4)_2SO_2$, m. $87-8^\circ$. From 142 g. MgI and 24 g. Mg in 400 cc. Et_2O with 48 g. $p\text{-MeC}_6H_4SO_2Cl$ in 300 cc. Et_2O are obtained only 2 g. $p\text{-tolylmercaptan methyl ether}$, refractive oil with narcotic odor, $b_{10} 104-5^\circ$, while the chief product is the disulfoxide. $PhSO_2Cl$ (25 g.) in 100 cc. Et_2O with 70 g. $PhBr$ and 10 g. Mg in 200 cc. Et_2O yields 1.5 g. Ph_2 , m. 71° , a very small amt. of an oil with unpleasant odor, $b_{10} 240-80^\circ$ (probably Ph_2S), and, as chief product, Ph_2SO , m. $70-1^\circ$. From 34.2 g. $p\text{-MeC}_6H_4SO_2Cl$ in 150 cc. Et_2O with 85 g. $PhBr$ and 12.9 g. Mg in 200 cc. Et_2O were obtained 2.5 g. Ph_2 and 15 g. of residue non-volatile with steam, crystg. from ligroin in needles, m. around 80° , which apparently consisted of a mixt. of $MeC_6H_4SO_2Ph$ and MeC_6H_4SOPh , and from which the pure sulfone, m. 124.5° , was isolated by fractional crystn. The aq. soln. of the reaction product contained $(MeC_6H_4SO_2)_2Mg$. α -Naphthyl- and camphormagnesium bromides reacted quietly with $MeC_6H_4SO_2Cl$ but no homogeneous products could be isolated. $p\text{-MeC}_6H_4SO_2Et$ (16 g.) in 75 cc. Et_2O with 5.7 g. Mg and 26 g. Et_2Br in 100 cc. Et_2O reacts without evolution of heat; after several hrs. the mixt., originally mobile, becomes viscous and is gently warmed for a short time; it is then decompd. in the usual way. The Et_2O soln. yields but a few drops of a yellowish oil with a penetrating odor, gives a cryst. ppt. in Et_2O with alc. $HgCl_2$. The main product is $(MeC_6H_4SO_2)_2Mg$ (18 g. of the hexahydrate).

CHAS. A. ROULLIER

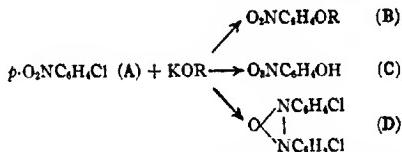
Rearrangement and saponification of toluene-*p*-sulfon-*p*'-anisidine and its *N'*-methyl derivative. J. HALBERKANN. Inst. f. Schiffs- u. Tropenkrankh., Hamburg. *Ber.* **54B**, 1665-75 (1921).—4-Methylbenzene-sulfonmethyl-4'-methoxyphenylamide (*N*-methyl-*N*-*p*-toluenesulfon-*p*-anisidine) (A), from 1 g. $MeC_6H_4SO_2NHCH_3OMe$ (B) in 3.65 cc. *N* NaOH and 6.5 cc. H_2O shaken with 0.46 g. Me_2SO or heated some hrs. on the H_2O bath with 0.68 g. $p\text{-MeC}_6H_4SO_2Me$ in 5 cc. MeOH, quadrangular prismatic columns from 75% alc., m. $68-9^\circ$, difficultly sol. in dil. acids and alkalies, sol. in H_2SO_4 (d. 1.84) without color but the soln. on standing in the air assumes a deep blue-violet color changed by a little H_2O into red and by H_2O into brick-red. When 16 g. A in 22 cc. H_2SO_4 (d. 1.84) and 8.5 cc. AcOH was heated on the H_2O bath it still gave a turbidity, even after 3 hrs., with H_2O and no increase in solv. was attained by gradually

raising the temp. up to 150°. After cooling, the mixt. was dild. with an equal vol. of H₂O and boiled 1 hr., still without any apparent change. The product was therefore poured into H₂O, whereupon the ptd. oil soon solidified; this was rubbed up, filtered, washed with dil. soda and H₂O, dried and crystd. from 500 cc. alc. after boiling with charcoal, yielding *p-tolyl z-methylamino-5-methoxyphenyl sulfone* (C), prisms, m. 150°, insol. in alkalies and cold dil. acids, shows a blue fluorescence in the solid state and in soln. in CHCl₃, Me₂CO, C₂H₅, AcOEt and alc. but not in AcOH, sol. in H₂SO₄ without color or fluorescence, easily sol. in hot HCl (d. 1.06-1.125). Neither A nor its isomer B is saponif. or otherwise changed by boiling 24 hrs. with alc. KOH or by heating alone 1 day at 160°. C (1 g.) in 5 cc. HCl (d. 1.125) and 30 cc. alc. treated in ice with 2 mols. NaNO₂, allowed to stand a long time and ptd. with H₂O gives *p-tolyl z-methyl-nitroamino-5-methoxyphenyl sulfone*, stout rhomboidal, partly almost cubical crystals from alc., m. 86-7°, gave in the Liebermann test first a green, then a permanent blue color, insol. in alkalies and dil. acids, shows a slight blue fluorescence when rubbed. *p-Tolyl z-methylacetylamino-5-methoxyphenyl sulfone*, from 2 g. C boiled 1 hr. with 5 cc. Ac₂O and a trace of concd. H₂SO₄, quadrangular needles from alc., m. 138°, insol. in dil. acids and alkalies. A rearrangement similar to that by which C is formed has been described by Witt and his pupils (cf. C. A. 9, 307), according to whom short heating with 80% H₂SO₄ at 135-50° brings about hydrolysis to MeC₆H₄SO₂H. H. found, however, that under these conditions there is complete rearrangement but that not a trace of *p-MeOC₆H₄NHMe* (D) is formed; systematic expts. in sealed tubes at 150°, beginning with 10% H₂SO₄, showed that up to 40% acid there is but little hydrolysis, most of the C being protected from attack by its slight solv.; 50% acid gave better results and the highest yield of D (60%) was obtained with 60% acid, the rest of the C (except for a small amt. decompd.) being partly unchanged and partly rearranged; 70% acid at 120° effected a complete rearrangement. According to W., the above rearrangement is limited to alkylated sulfonamides, sulfonamides of primary bases undergoing only cleavage and the resulting amine often being simultaneously sulfonated. H., however, has succeeded in effecting the rearrangement of the non-alkylated B, 10 g. of which heated 1 hr. at 150° with 40 cc. of H₂SO₄ (d. 1.84) and poured into ice H₂O gave 3.5 g. 2,5-HO(H₂N)C₆H₃SO₂H (E), needles, turn faintly violet about 270°, then darken and gradually carbonize above 300°, reduce cold AgNO₃ and hot Fehling soln., couple with β-naphthol in soda after diazotization, give quickly with FeCl₃ through reddish brown and violet, a deep blue color and then slowly, a violet-red color. If the needles are dissolved in just the necessary amt. of boiling H₂O the E soon seps. in cubes or quadratic and rectangular tablets followed on long standing in the cold by needle druses from which radiate long hair-like needles. The tablets are anhydrous, the needles contain 1 H₂O. The H₂SO₄ filtrate from the E, extd. with much Et₂O, yields *p-tolyl z-amino-5-methoxyphenyl sulfone*, stout, slightly reddish yellow prisms from alc., m. 148°, insol. in alkalies and dil. acids, easily sol. in HCl of d. 1.06 and repprd. by H₂O gives an olive brownish ppt. with FeCl₃ in alc.; the best yield (35%) is obtained by heating 1 g. B 1 hr. at 110° with 3 cc. of 80% H₂SO₄; acid of d. 1.84 at 93° gives only 3.5%. The hydrochloride slowly seps. from the soln. in cold acid nf d. 1.06 in long, pointed, quadrangular needles. *Acetyl derivative*, stout quadrangular needles from dil. alc., m. 134°. The following azo compds. were prep'd. by diazotizing the sulfone in dil. Me₂CO, coupling the phenols in soda, the *m-C₆H₄(NH₂)₂* in HCl, and, in the last case, ptdg. with soda. *Bis-1,3-[4'-methoxy-2'-p-toluenesulfonylbenzeneso] -4,6-dihydroxybenzene*, [MeO(MeC₆H₄SO₂)C₆H₃N: N₂C₆H₄(OH)₂], seps. as a by-product from the soln. of the monoazo dye in boiling AcOH on cooling in fine, orange-red needles, darken above 250°, m. 272° (decompn.), insol. in aq. alkalies, easily sol. in alc. alkalies with deep red color and completely repprd. by H₂O, sol. in

H_2SO_4 (d. 1.84) with violet-red color; when the mother liquors are dild. with H_2O and the ppt. is dissolved in NaOH and treated with HCl there is obtained 4'-*methoxy-2'-p-toluenesulfonylbenzenazo-2,4-dihydroxybenzene*, stout, brown-red needles from dil. AcOH, m. 219°, sol. in H_2SO_4 with deep brown-red color. 4'-*Methoxy-2'-p-toluenesulfonylbenzenazo-2-naphthalene*, bright red quadrangular needles from alc., m. 203°, insol. in alkalies sol. in H_2SO_4 with $KMnO_4$, color changing to reddish blue with a trace of $FeCl_3$, in org. solvents with red-brown color changed by NaOH to deep red, the Na salt (which is almost insol. in H_2O) remaining in soln. in the org. solvent (except Et_2O). 4'-*Methoxy-2'-p-toluenesulfonylbenzenazo-2,4-diaminobenzene*, dark viscous mass with green shimmer; *hydrochloride*, stout violet-red needles from dil. alc. The H_2SO_4 soln. is brown-red with a violet tinge. *p-Tolyl 2-amino-5-hydroxyphenyl sulfone*, from the Me ether heated several hrs. at 150° with 10 parts HCl (d. 1.125), taken up in H_2O , treated with excess of NaOH, freed from the unchanged Et_2O with $CHCl_3$, acidified with HCl, made alk. with soda and repeatedly extd. with Et_2O , stout prismatic columns from C_6H_6 , m. 150°, easily sol. in alkalies, shows a blue fluorescence both in the solid state and in soln., couples with diazotized amines and, after diazotization, with phenols, gives with $FeCl_3$ in alc. an olive-brown color passing through greenish.

CHAS. A. ROUILLER

The preparation of nitrophenetole from nitrochlorobenzene. A. V. BLOM. Söderläje. *Helvetica Chim. Acta* 4, 297-318 (1921); cf. *Ber.* 8, 1626 (1875); 15, 1002 (1882).—The mechanism of the following reaction was studied:



The rate of reaction to form B and C can be followed by a Cl-ion detn., using Volhard's method; this is designated as the Ag titer. During the reaction the alkalinity of the soln. is reduced with the formation of two neutral compds. and the acidic C, thus affording a means of following the rate of reaction by using different indicators. The reaction is made more complicated by the fact that free alkali is used in the formation of D:



Phenolphthalein, brilliant yellow and Congo red were used as external indicators and the results designated as Ph titer, Br titer and Ko titer, resp. The results thus obtained give the following information: Ag, B and C; Ko, B and D; Ph, B, C and D; Ph + Ag, D; Ko - Ph, C. The accuracy of this analysis was checked by isolation of the reaction products; H_2O is added, the alc. removed by distn., halogen-free HNO_3 added to neutralize the residue and steam distd. to remove A and B. The Cl ion in the steam-distd. residue was detd. on an aliquot and found to be somewhat less than when detd. directly on the original reaction material because of solidification in the pipet and the coeff. of expansion. D seps. quant. from the steam-distd. residue on cooling; after filtering and making acid with H_2SO_4 , o-nitrophenol is removed with steam; *p*-nitrophenol was usually isolated by evapn. of the distn. residue and recrystn. from concd. HCl. Better results were sometimes obtained by dissolving the crude *p*-nitrophenol in *N* NaOH and titrating the excess alkali although the resinous impurities do not react neutral and interfere with the titration. A mixt. of 0.1 mol. of A in hot Et_2O and 0.1 mol. c. p. KOH was placed in a thermostat under a reflux condenser. To det.

the influence of concn. three different solns. were made with different amts. of EtOH and H₂O. At regular intervals, 5 cc. portions were removed and titrated with 0.1 N HNO₃ to obtain the Ph, Br, and K₂CrO₄, after which K₂CrO₄ was added to the neutral soln. and titrated with 0.1 N AgNO₃ to obtain the Ag titer. The concns. used were: 0.1 mol. A, 170 cc. EtOH and 44 cc. H₂O (X); 0.1 mol. A, 120 cc. EtOH and 80 cc. H₂O (Y); 0.1 mol. A, 240 cc. EtOH and 160 cc. H₂O (Z). The results for the different concns. and temps. were tabulated and plotted on logarithmic paper. It was found that at 60° the reaction is very slow, 0.5 having reacted after 115 hrs. At 70° the rate of reaction increases rapidly; 50% of the Cl had been displaced after 44 hrs. with concn. Y and with concn. X after 20 hrs. At the boiling point of the mixt. the concn. of the reacting substances has very little influence and a curve is obtained which lies between the curves for X and Y at 70°, cutting the latter at 110 hrs., after which it rises very slowly; 0.5 of the reaction is complete after 29 hrs. and at 150 hrs. the amts. of the reaction products remain almost const. The yields at the b. p. are less satisfactory than at lower temps. To calc. the amt. of D formed during the time from *t* to *t'*, the following formula is used: [(Ph + Ag)titer at *t* — (Ph + Ag)titer at *t'*] × 1.7 = azoy % . When the Br titer is used in place of the Ph titer the result must be multiplied by 2 as the Br titer is influenced in this reaction by the presence of D. The reason that the % of KCl does not continuously increase after 150 hrs. at the b. p. of the reaction is due to the formation of about 20% D, which does not have the Cl in a reactive form, and at the same time a corresponding part of the free alkali is used in the formation of KOAc, thus removing KOH from the reaction. It was found that at 70° the rate of reaction varies indirectly as the amt. of solvent and directly with the concn. of the alc. The relative concn. between B and C is not noticeably changed by such a variation in the solvent. The same was found to be true at 50° and 60°. PhII in place of H₂O for diln. was found to reduce to a high degree the rate of reaction and yielded about three times as much of D as in the corresponding expts. using H₂O. When Me₂CO was used to replace the H₂O considerable amts. of tar and resinous material were formed. The following catalysts were tried and found to have no favorable influence: Cu, CuI, I, HgO and HgI₂. When NaOH is used to replace KOH the results are almost identical; if 1 mol. excess alkali is used the rate of reaction is increased but about twice as much C is formed and after 47 hrs. 34% of D is present; if the 1 mol. excess alkali is added gradually during the reaction the yield of B is somewhat better. If the free alkali is replaced by 1 to 3 mols. of carbonate the reaction is decidedly slower. o-O₂NCH₂Cl was found to yield the same results as A except that the velocity of reaction is much less; curves are given for comparison with A under the same conditions. From a kinetic study of the reaction it was found that at temps. below 70° the reaction is bimol., while at the b. p. it is of the third order. The consts. for the reaction are tabulated and from them it is possible to calc. the amt. of A which has reacted after any interval of time.

N. A. LANGE

Synthesis and dehydration of ethylpropylphenylcarbinol. VARTAKS YÉRAMIAN.

Compt. rend. 173, 362-4 (1921).—By dropping BzPr into EtMgI in Et₂O, and decomp., with ice, a crude product is obtained contg. *ethylpropylphenylcarbinol*, most of which is found in the fraction b.p. 132°. No phenylurethan of this alc. could be prepd., on account of the ease with which it loses H₂O, giving a deriv. of C₆H₅. Complete dehydration takes place on passing the vapors over infusorial earth heated to dull redness, giving a liquid, b. 216°, having the formula C₁₀H₁₂, which decolorizes Br water, and gives a nitrosoate with a very low m. p. Oxidation by CrO₃ in AcOH gave EtBz (semicarbazone m. 175°), showing that the unsatd. hydrocarbon consists at least in part of *3-phenyl-3-ketene*. EtCH=CPhEt.

M. R. SCHMIDT

Compounds of sulfuric acid with the chloride and anhydride of benzoic acid.

MAX BERGMANN AND FRITZ RADT. Kaiser-Wilhelm-Inst. f. Faserstoff-Chem., Berlin-Dahlem. *Ber.* 54B, 1652-5 (1921).—It has long been known that acetylation with Ac₂O or benzoylation with BzCl or Bz₂O is accelerated by small amts. of H₂SO₄ and it has often been assumed that this is due to the intermediate formation of mixed anhydrides of the CO₂H acid and the H₂SO₄, but thus far no such products have been isolated. It has now been found that if 5 g. BzCl in 3 cc. dry CHCl₃ is treated with 3.4 g. anhydrous H₂SO₄ an addition product begins to sep. in a few min. in long prismatic needles or more compact crystals; these are filtered with gentle suction, washed with CHCl₃-CS₂ and then with CS₂ (care being taken that they never become entirely dry and exposed to the moisture of the air) and dried in a P₂O₅ desiccator; yield, 55%. Under these conditions they are stable for several days, m. 52-3°, have the compn. C₇H₅ClO₄S, are instantly decompd. by H₂O with formation of BzOH, can be recrystd. unchanged from dry CHCl₃ and other iodine-free solvents but at once evolve gas with moist solvents, give BzCl and ClSO₃H with PCl₅. Bz₂O (8 g.) in 4 cc. CS₂ with 3.3 g. H₂SO₄ similarly gives 92% of a compound C₇H₅O₃S, needles or prisms, m. about 70-2°. That Oppenheim (in 1870) observed the evolution of HCl and obtained a compd. BzSO₃H by the action of H₂SO₄ on BzCl was probably due to his using moist H₂SO₄, the H₂O in which immediately decompd. the primary addition product. In view of Aschan and Europäus' observation that AcCl and anhydrous H₂SO₄ evolve no HCl (*C. A.* 7, 3328) B. and R. are inclined to believe that AcOH derivs. behave like those of BzOH with H₂SO₄.

CHAS. A. ROULLER

Action of methyl and ethyl alcohols on the esters of 2,6-dinitro- and 2,4,6-trinitrobenzoic acids. J. J. SUBBOROUGH AND D. D. KARVÉ. *J. Indian Inst. Sci.* 4, 177-80 (1921).—It is shown that when the esters of di-*o*-nitrobenzoic acids are heated with alcs. at 180° the CO₂Me and CO₂Et groups are replaced by H, producing the corresponding nitrobenzene, CO₂ and the ether. 2,6-(O₂N)₂C₆H₃CO₂Me heated 100 hrs. in a sealed tube at 180° with 10 parts EtOII and evapd. to crystn. gave 2 fractions, yellow needles, m. 80-2° and 65-7°, both of which were identified as *m*-C₆H₄(NO₂)₂ by conversion into the benzidine and α -C₆H₄NH₂ addition compds., m. 125° and 55-6°, resp. When 2,6-(O₂N)₂C₆H₃CO₂Et was treated in the same way and the gases were condensed with liquid air, the odor of Et₂O was noticed and 16% of the gas proved to be CO₂. 2,4,6-(O₂N)₃C₆H₂CO₂Me (1 g.) similarly treated, with 10 cc. alc. gave 2,4,6-C₆H₃(NO₂)₃, quant.

BENJ. V. BUSH

Esters of aminobenzoic acids. HARVEY C. BRILL. *J. Am. Chem. Soc.* 43, 1320-3 (1921).—The aminobenzoic esters were in general prep'd. from the NO₂ esters with Sm and HCl below 35° and roughly classified as to their relative anesthetic power (detd. by placing a small amt. of the ester on the tongue) into 3 groups: most powerful (a), intermediate (b) and least powerful (c). Below are their properties: *Allyl p*-aminobenzoate, m. 52° (a); HCl salt, plates, m. 180°. *Isopropyl ester*, m. 79° (a); *hydrochloride*, coarse needles, m. 184°. Bu ester, m. 58° (a); HCl salt, coarse needles, m. 198°. *Butyl m*-aminobenzoate, m. below 0°, h. 245° (b); *hydrochloride*, plates, m. 128°. *o*-*Isomer*, m. below 0°, h. 182° (b); *hydrochloride*, needles, m. 178°. Et 3,5-diaminobenzoate, m. 84° (b); HCl salt, plates, m. 248°. *Butyl ester*, m. below 0°, h. 255° (a); *hydrochloride*, needles, m. 253°. *2,4-Isomer*, m. 90° (c); *hydrochloride*, needles, blackens 270°. Of the intermediate NO₂ esters, the allyl *p*-nitrobenzoate and Bu *m*-aminobenzoate are liquids; iso-Pr *p*-nitrobenzoate m. 95°; the Bu ester m. 35°; Et 3,5-dinitrobenzoate m. 91°; the Bu ester m. 61°; and the 2,4-isomer m. 70°.

CHAS. A. ROULLER

The *o*-diethylaminocyclohexanol ester of *p*-aminobenzoic acid. A. E. OSTBERG AND E. C. KRNDALL. *J. Am. Chem. Soc.* 43, 1370-1 (1921).—*o*-*D*iethylaminocyclohexyl *p*-aminobenzoate (A) was synthesized with the idea of maintaining those linkages

($-\text{OCH}_2\text{CH}_2\text{N}=\text{}$) in procaine, $\rho\text{-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{CH}_2\text{CH}_2\text{NEt}_3$, to which its physiol. action is ascribed and at the same time materially increasing the mol. wt. The physiol. properties of A and of several of its derivs. with substituents in the cyclohexane ring will be described elsewhere. *o-Diethylaminocyclohexanol*, from 54 g. *o-chlorocyclohexanol* and twice the caled. amt. of NHET_3 , heated several hrs. at 150° , $b_{10} 224^\circ$; *hydrochloride*, m. 160° . *p-Nitrobenzoate*, from 17 g. of the alc. slowly added to 20 g. $\rho\text{-ONC}_6\text{H}_4\text{COCl}$ in Et_2O , is isolated as the *hydrochloride*, m. 175° (yield, 80%), which with Sn and concd. HCl at about 35° yields A, plates, m. 72° ; *monohydrochloride*, m. 163° .

CHAS. A. ROUILLER

Nitro and amino derivatives of *m*-hydroxybenzoic acid. VICTOR FROELICHER AND JULIUS BERND COHEN. Univ. Leeds. *J. Chem. Soc.* 119, 1425-32 (1921).—An attempt to repeat Griess's work (*Ber.* 20, 405) on 2,3-O₂N(HO)C₆H₄CO₂H was unsuccessful, 4-, 5- and 6-NO₂ acids being obtained but no 2-NO₂ acid. The disadvantage of the method is the resinous nature of the product. HO₂CC₆H₄OAc cannot be nitrated with HNO₃ alone, but in the presence of H₂SO₄, hydrolysis occurs, followed by nitration. MeO₂CC₆H₄OH may be nitrated in CCl₄ with fuming HNO₃, but the yield is poor. MeO₂CC₆H₄OMe is still more difficultly nitrated. Most satisfactory results were obtained with HO₂CC₆H₄OMe, of which 50 g. were added to 400 cc. Ac₂O, cooled and then treated with a mixt. of equal vols. of fuming HNO₃ (24 g.) and concd. H₂SO₄ at -5 to -10° for 8 hrs.; yield 50 g. mixed NO₂ acids, the main product being the 4-acid, with smaller quantities of the 2-acid. The MeO group differs to some extent from the HO group in its directing influence. 4,3-H₂N(HO)C₆H₄CO₂H was prepd. according to Einhorn (*Ann.* 311, 43), m. $115-6^\circ$. *4-Carbamido-m-hydroxybenzoic acid*, from 5 g. of the NH₂ acid, 2.5 g. KCN and 10 cc. H₂O, m. 308° , with evolution of NH₃. *4-Carboxyamino derivative*, C₉H₁₁O₃N, leaflets, m. $250-2^\circ$. *4-Amino-m-methoxybenzoic acid*, leaflets, m. $185-6^\circ$. *Hydrochloride*, not very sol. in H₂O. *Acetate*, m. 271° . *4-Carbamino derivative*, m. 228° . *4-Carboxyamino derivative*, m. $201-3^\circ$. *2-Amino-m-methoxybenzoic acid*, slightly brown leaflets, m. $170-1^\circ$. *Acetate*, needles, m. 208° . *2-Carbamido derivative*, leaflets, m. 160° . On boiling with HCl, the *hydantoin*, MeO₂C₆H₄CO.NH.CO.NH is formed, m. $258-9^\circ$. *2-Carboxyamino*

derivative, leaflets, m. $152-4^\circ$. *Methoxy- γ -hydroxyquinaldine- β -carboxylic acid*, by boiling the acid with excess of AcCH₂CO₂Et, m. 270° . *6-Carbamido-m-hydroxybenzoic acid*, small prisms from AcOH, m. $166-7^\circ$ (decompn.). The *hydantoin* sublimes above 360° .

C. J. WEST

The power of addition of some styrene derivatives. S. REICH, R. VAN WIJKEK AND C. WAHLLE. *Helvetica Chim. Acta* 4, 242-9 (1921).—In a previous work (cf. *C. A.* 15, 513), the speed of addition of Br to the chlorocinnamic acids was studied with the object of detg. the influence of the halogen on the addition power of the double bond. The present research was undertaken to establish what influences, if any, the mass or vol. as well as the chem. nature of the substituent has on the same property. The study was made on derivs. of styrene obtained by substituting the terminal CH₃ of the side chain. These derivs. consisted of 2 groups of compds.: (1) those having alkyl radicals of electropositive character but differing in mass and vol. and, (2), those in which the radical introduced was of electronegative nature as Br, Ph, CN and CO₂H. The 1st group contained 9 hydrocarbons, all prepd. by a uniform method depending on the following steps: (a) formation of sec. alcs. by Grignard's reaction; (b) conversion of the alcs. to Cl derivs. by treating with HCl gas at 0° ; and (c) heating the latter with pyridine at 125° to eliminate HCl and form the styrene derivs. In many cases, (d) it was possible to obtain the styrene compds. directly from the sec. alcs. by simple warming for several min. with H₂SO₄ of d. 1.50. In the course of the study, 5 new

hydrocarbons were synthesized. The action of iso-AmMgBr on BzH gave *phenylisoamylcarbinol*, b_{11} 132°, which by steps (b) and (c) was converted to *isobutylstyrene*, b_{11} 107–9°, (rectified *in vacuo* over Na), liquid of agreeable odor. *Phenylisohexylcarbinol*, obtained by treating 2-chlorohexane in Et_2O with Mg and then warming with BzH, is a liquid of slightly oily consistency, b_{11} 144–5°, d_{17} 0.9574, n 1.50310. By step (d), the latter was transformed into *methylbutylstyrene*, mobile liquid, possessing an odor recalling pine-cones, b_{11} 114–6°, d_{17} 0.8974, n 1.51505. The action of the Mg compd. of 1-chlorohexane on PbCH_2CHO yielded *benzylhexylcarbinol*, oily liquid with a feeble but agreeable odor, b_{11} 163–5°, d_{17} 0.9348, n 1.50151, which on warming with H_2SO_4 gave *hexylstyrene*, b_{11} 136–8°, d_{17} 0.9063, n 1.50728. *Benzylcyclohexylcarbinol*, prep'd. from PhCH_2CHO and the Mg compd. of chlorocyclohexane, is a cryst. compd., m. 60°, b_{11} 175–7°, insol. in H_2O and readily sol. in alc. and Et_2O . By operation (d), *cyclohexylstyrene* was obtained therefrom, colorless liquid of agreeable odor, b_{11} 145–7°, d_{17} 0.9595, n 1.53701. Oxidized with KMnO_4 , it yielded a mixt. of BzOH and hexahydrobenzoic acids. The reaction between BzH and the Mg compd. of chlorocyclohexane gave *phenylcyclohexylcarbinol* previously described by Sabatier (cf. *Compt. rend.* 139, 345(1904)), which by step (d) was transformed into *benzylidenecyclohexane*, liquid of anise-like odor, b_{11} 122–3°, d_{17} 0.9640, n 1.53950. The affinity of these hydrocarbons for Br was measured by mixing 0.15–0.20 g. of each compd. in 10 cc. dry CS_2 and the theoretical amt. of Br in 10 cc. of the same solvent in a stoppered flask, agitating and setting it aside for a detd. length of time (for each hydrocarbon to detns. were made, one for 1 min. and one for 13 min.). At the end of each period, the excess Br was detd. by titrating the I liberated from KI. From the results obtained, the authors deduce that, (1) the affinity of styrene for Br is slightly augmented by the substitution of alkyl radicals for the H of the CH_3 group, the electro-positive nature of the alkyl facilitating the entrance of a negative element; double substitution is as advantageous as single; (2) the lengthening of the straight chain of the alkyl lowers the power of addition; (3) the power of addition seems to remain the same when the straight chain is replaced by a branching one; (4) the cyclic form of the side chain increases this property. The chemical nature of the substituents being the same, the observed differences in the power of addition of these compds. is attributed to stereochem. factors connected with the mass or vol. of the groups in the vicinity of the double bond. The compds. of the 2nd group containing different electronegative elements were prep'd. according to known methods. The affinity for Br was measured similarly as for the 1st group excepting that in some instances it was necessary to extend the time of contact with Br to 72 hrs. in order to obtain an appreciable amt. of added Br. The results showed that, (1) the replacement of an alkyl by a Pb radical diminishes considerably the power of addition; (2) the substitution of a H of the C_6H_5 nucleus with a MeO group increases the capacity for addition; (3) the introduction of a halogen into the nucleus lowers this power but much less so than CN does; (4) the CO_2H group has a particularly depressing effect approaching that of CN; (5) esterification largely counteracts the influence of the CO_2H ; (6) double substitution by the preceding atoms or radicals abolishes almost entirely the power for addition. In general, the affinity of the substituted styrenes for Br is in inverse ratio to the electronegative character of the substituent.

A. T. FRASCATI

A chemical investigation of the asphalt in the tar sands of northern Alberta. VERNON K. KRIEBLE AND WILLIAM F. SEYER. *J. Am. Chem. Soc.* 43, 1337–49(1921).—The sample of asphalt studied, freed from sand, was of the semiliquid variety classed by Richardson as maltbas, with d_{10} 1.022, penetration at 20° 0.00, sol. to the extent of 100% in CS_2 , CCl_4 , CHCl_3 , concd. H_2SO_4 and concd. HNO_3 (after several days in the last 2 cases), 98% in C_6H_6 , 86.9% in hot Et_2O , 70% in hot Me_2CO and 33% in hot alc.,

with 2.0, 22.5, 24.9 and 51.5%, resp., of saponifiable matter, asphaltenes, resins and oily constituents, and 2.74, 84.49, 11.23 and 0.04%, resp., of S, C, H and N. By extg. the tar sand with petr. ether (b. below 55°) and filtering through fuller's earth, there was obtained a light red, transparent oil with d₂₀ 0.927, n_D 1.5000, a 1.5–1.6°, viscosity at 20° 20.0, mol. wt. 350.0, containing 1.87, 85.76 and 12.10% S, C and H, resp., and with an I no. of 2.1. This on fractionation in a special distg. app. (a drawing of which is given) evacuated by means of a Maass H₂SO₄ pump (*C. A.* 15, 453) and purification of the distillates with liquid SO₂ yielded the following 13 apparently pure hydrocarbons (the values following the b. p. give d₂₀, n_D, and the rotation in a 1-dm. tube, resp.): C₁₁H₁₆, b₁₀ 75–80°, 0.8186, 1.4450, 0.0°; C₁₃H₁₆, b₁₀ 95–9°, 0.8395, 1.4580, 0.14°; C₁₃H₁₆, b₁₀ 81–1°, 0.8558, 1.4640, 0.15°; C₁₃H₁₆, b₁₀ 90–3°, 0.8632, 1.4681, 0.17°; C₁₃H₁₆, b₁₀ 95–8°, 0.8723, 1.4722, 0.18°; C₁₅H₁₆, b₁₀ 107–10°, 0.8751, 1.4778, 0.17°; C₁₅H₁₆, b₁₀ 122–5°, 0.8833, 1.4820, 0.22°; C₁₅H₁₆, b₁₀ 133–5°, 0.8889, 1.4768, 0.23°; C₁₅H₁₆, b₁₀ 143–7°, 0.8926, 1.4859, 0.30°; C₁₅H₁₆, b₁₀ 153–6°, 0.8977, 1.4911, 0.30°; C₁₅H₁₆, b₁₀ 158–62°, 0.9020, 1.4942, 0.48°; C₁₅H₁₆, b₁₀ 183–4°, 0.9180, 1.5011, 0.76°; C₁₅H₁₆, b₁₀ 220–5°, 0.9132, 1.5180, 1.21°. The compns. of these compds. were confirmed by C and H dectns. and mol. wt. measurements in freezing C₂H₄ and the mol. refraction indexes and the mol. vols. indicate that no double bonds are present.

CHAS. A. ROUILLEK

Dicyclohexylamine and cyclohexylaniline. G. FOUGÉ. *Ann. chim.* 15, 291–32 (1921).—F. presents a very thorough study of *dicyclohexylamine* (A) and *cyclohexylaniline* (B), describing in detail the method of prepn. of the compds. in a pure state and the physical and chem properties of each. In its reactions A behaves like a sec. amine of the aliphatic series while B resembles more closely the aromatic amines. Probably the most outstanding characteristic of A is the great aptitude it possesses to form addition compds. even with such neutral compds. as H₂O and alc. This property is shown to only a slight degree by B. *Method of prepn. of the pure compds.* PhNHH₂ was hydrogenated in the presence of reduced Ni according to the method of Sabatier and Senderens (*Compt. rend.* 138, 457 (1904)). The product thus obtained is a mixt. of about 33% of cyclohexylamine, 10% unconverted PhNHH₂, 33% of A and B in about equal ratios, some C₆H₆, C₆H₅, and a small quantity of PbNHH₂ and tarry substances. The method of sepn. of A and B from the crude product (described fully in the original) depended mainly on fractional distn. at atm. pressure and *in vacuo*, removal of A through its *bicarbonate* from the rectified product and extn. with dil. H₂SO₄ to isolate B, which forms a sol. *sesquisulfate*. The final purification of each compd. was made by distg. under reduced pressure. *Physical properties of A.* Pure A is a liquid of slightly oily consistency and somewhat unpleasant odor, b. 135°, 142°, 156° and 252° under 20, 30, 52 and 754 mm., resp. (S. and S. gave b. 250° and b₁₀ 145°.) After drying *in vacuo* over BaO and P₂O₅, it shows d₁₀ 0.917 and n_D 1.488. A is almost insol. in H₂O but miscible with alc. and most. org. solvents. *Chemical properties of A and its principal derivs.* With H₂O at a temp. <23°, A forms a *hydrate* (C), (C₆H₁₁)₂NH·H₂O, white, cryst. mass, m. 23°; soly. in H₂O, 0.21% at 11°. C is a strong base which displaces NH₃ from its salts, and gives with solns. of metallic salts generally the same ppt. as KOH and NH₄OH. In contact with the vapors of EtOH, A adds 1 mol. of the alc., giving the *alcoholate*, (C₆H₁₁)₂NH·EtOH, pearly white crystals, m. 28°, which darkens on standing and dissociates in the air. *Dihydrofluoride* (D), obtained by concg. A in an excess of HF and cooling, forms prisms, decomp. >300° without melting, very sol. in H₂O, sol. in alc., tarnishes rapidly with loss of HF and attacks glass. The neutral *hydrofluoride*, obtained by further evapg. the soln. of D and cooling, seps. in microencellles, sublimes with partial decompr. on heating, is sol. in H₂O and alc., loses HF gradually and attacks glass. By treating a soln. of the *bicarbonate* with HCl or the neutral

sulfate with BaCl_2 , the *hydrochloride* (E) is formed, fine needles, decomp., without melting about 350° , difficultly sol. in cold H_2O but very sol. in boiling H_2O and in alc., almost insol. in CHCl_3 and Et_2O . The *hydrobromide*, prep'd. similarly to E , fine needles, slightly sol. in cold H_2O , sol. in boiling H_2O , very sol. in hot alc. and difficultly sol. in Et_2O , decomp., about 350° . KI and the neutral sulfate give the *hydroiodide* micro platelets, very slightly sol. in cold H_2O , more sol. in boiling H_2O , sol. in warm EtOH and MeOH , slightly in CHCl_3 and quite insol. in Et_2O , decomp. above 300° . An aq. soln. of the bicarbonate in H_2O , neutralized to litmus with H_2SO_4 , evapd. at 90° to crystn., and cooled, yields the neutral *sulfate* (F) which, recrystd. from alc., has the formula $2(\text{C}_4\text{H}_{11})\text{NH}.\text{H}_2\text{SO}_4.\text{H}_2\text{O}$. F forms quadratic crystals, remains neutral in the air but becomes acid over H_2SO_4 , becomes opalescent at 95° , loses H_2O , then amine but gives no definite compd. Its solv. in H_2O rises from 24 g. in 100 g. at 0° to 41 g. in 100 g. at 88° . F is sol. to the extent of 35% in cold 90% alc. and 60% at the h. p. Recrystd. from a hot, satd. alc. soln. it contains alc. of crystn.; it is insol. in Et_2O . Evapn. of the slightly acid soln. of the neutral sulfate to crystn. and cooling yields the *sesquisulfate*, $3(\text{C}_4\text{H}_{11})\text{NH}.2\text{H}_2\text{SO}_4$, needles, m. 187° , almost insol. in Et_2O but sol. in H_2O and alc. The *bisulfate*, prep'd. by cooling a hot aq. soln. of F to which an equiv. of H_2SO_4 has been added, forms hygroscopic needles, m. 182° , much less sol. in H_2O than the other sulfates but sol. in an excess of concd. H_2SO_4 , very sol. in alc. and nearly insol. in Et_2O . The *nitrile*, obtained from F and $\text{Ba}(\text{NO}_3)_2$, plates, decomp., quickly on heating, very sol. in cold H_2O and alc., more so in hot alc. and CHCl_3 , and insol. in Et_2O . The direct action of H_3PO_4 on A produces the *monobasic phosphate*, octahedrons, m. 225° , decomp. at higher temps., sol. in H_2O and alc. By passing moist CO_2 into A in petr. ether or by the action of CO_2 on C , the *bicarbonate* (G) is formed as a white, silky mass of interlaced microneedles, m. 61° (decompn.), sol. in H_2O with alk. reaction to litmus but acid to phenolphthalein, slightly sol. in Et_2O , insol. in petr. ether and sol. in alc. (with decompn.). When a concd. soln. of F is treated with concd. K_2CrO_4 , the neutral *chromate* (H), $2(\text{C}_4\text{H}_{11})\text{NH}.\text{H}_2\text{CrO}_4$, is obtained as a citron-yellow powder, decomp. $>100^\circ$, difficultly sol. in H_2O , sol. in alc. and in CHCl_3 , insol. in Et_2O and in benzene. The alc. soln. decomp. rapidly with the formation of a brown ppt. A very gradual addition of dil. H_2CrO_4 to a soln. of F yields the *dichromate* (I), deep orange-red, quadratic or rectangular plates, darkens in contact with the mother liquor and decomp. rapidly on heating, slightly sol. in H_2O , sol. in alc. and especially in CHCl_3 , insol. in Et_2O and benzene. The alc. soln. decomp. similarly to that of H . The *trichromate* (L), $2(\text{C}_4\text{H}_{11})\text{NH}.\text{H}_2\text{Cr}_2\text{O}_7$, prep'd. by adding a soln. of F at the rate of a few drops per day to dil. $\text{H}_2\text{Cr}_2\text{O}_7$ forms very dark brownish red prisms, difficultly sol. in H_2O , sol. in alc. and CHCl_3 , insol. in Et_2O and benzene, behaves like I towards heat and in alc. On evapg. in the cold a soln. of A in a slight excess of dil. AcOH , the *acetate* is readily obtained in the form of silky, white needles, m. 65° , very sol. in H_2O , alc., Et_2O and org. solvents; on strong heating it dissociates with partial decompn. Heating with Ac_2O was necessary to transform it into *dicyclohexylacetamide*. The *acid oxalate*, formed when A is added to $(\text{CO}_2\text{H})_2$ in boiling alc. and cooled, seps. as very refringent, prismatic needles, m. 206° , sol. in cold and hot H_2O , and in hot alc. The *picrate*, easily prep'd. by satg. hot alc. with A and picric acid taken in equiv. quantities and cooling the soln., seps. as beautiful, yellow prisms, m. 173° , difficultly sol. in cold H_2O , more sol. in hot H_2O , by which it is slowly hydrolyzed, sol. in alc., particularly when hot. Certain compds. as CH_3Ac , PhOH , quinol and α -and β - $\text{HOCH}_2\text{CH}_2\text{NO}_2$ react with A , giving solid products. The latter, however, could not be obtained in a pure state by crystn. for the purpose of analysis. When A in CS_2 was evapd., a residue of light yellow crystals was obtained believed to be *dicyclohexylamine dicyclohexylthiocarbamate* (M), $(\text{C}_4\text{H}_{11})\text{NCSNH}-$

$(C_6H_{11})_2$, long, prismatic lamellas, m. 111°, insol. in cold H_2O ; boiling H_2O and alk. solns. seem to decompose it; HCl converts it to E; it is readily sol. in alc., Et_2O and $CHCl_3$ with partial dissociation. The action of KNCO on F yields the unsym. *dicyclohexylurea*, $(C_6H_{11})_2NCONH_2$, microneedles, m. 247°, slightly sol. in H_2O , sol. in alc. and Et_2O . Warmed with HCl, it gives CO₂, NH₄Cl and E. S. and S. (*Ann. chim. phys.* [8] 4, 379 (1905)) have prep'd. the *phenyldicyclohexylurea*, white needles, m. 169°. MeI reacts on A with evolution of heat, giving a mixt. of *dimethylidicyclohexylammonium iodide* (M) and A·HI. M crystallizes in prisms, m. 216° (decompn.), slightly sol. in cold and very sol. in hot H_2O . On the other hand, the product from the action of EtI on A contains only a small amt. of the quaternary iodide, being constituted almost entirely of *ethyldicyclohexylamine hydroiodide*, a difficultly sol. salt, whose free base (O) is an oily liquid, b. 273°. *Diethyldicyclohexylammonium iodide*, readily obtained from O by warming the latter with a slight excess of EtI, tabular crystals, m. 224°, very sol. in H_2O and alc. Cl acts on A producing E and *dicyclohexylchloramine* (P), better prep'd. by treating A or a concd. soln. of G with a concd. soln. of pure HOCl. P sepa. in pale yellow, microlamellas of sharp, affluous odor, m. 26°, insol. in H_2O and sol. in concd. H_2SO_4 and org. solvents. Many of the chem. properties of P are described. When $NaNO_3$ is added to F in alc. acidified with H_2SO_4 , *dicyclohexylnitrosamine* is formed, pale yellow crystals, m. 105°, slightly sol. in H_2O but very sol. in alc., Et_2O , $CHCl_3$ and ligroin. *Dicyclohexylacetamide* (from A with a large excess of Ac₂O), crystallizes in prisms, m. 102°, insol. in cold or hot H_2O , very sol. in alc., Et_2O , AcOEt and $CHCl_3$. SCl with A forms a viscous, uncyclizable product. Attempts to prep. tetracyclohexylurea by the action of COCl₂ on A failed, some E and a viscous, uncyclizable mass being the only products. From A with BiCl₃ on the H_2O bath, a mixt. of E and *dicyclohexylbenzamide* was obtained. The latter crystallizes from Et_2O in prisms, m. 77°, insol. in H_2O and sol. in alc. and $CHCl_3$. When A or its sulfate is heated with concd. or fuming H_2SO_4 for 15 hrs., it is converted into $(NH_4)_2SO_4$. The thermal decompn. of A yields B, H₂ and tarry substances. *Quant. detn. of A*. The sulfates of A are sol. but not hydrolyzable. Hence, if A is in the free state or present as the hydrate, its quant. estn. can be made by dissolving in an excess of H_2SO_4 and titrating the excess with litmus. The HCl salt of A is a well defined salt, difficultly sol. in H_2O , not hydrolyzable and can be dried at 110° without volatilization or decompn. It is therefore well adapted for the detn. of A when the latter is combined with volatile acids. The salt is treated with an excess of HCl, evapd. to dryness, dried at 110°, cooled and weighed. The sepn. of A for analytical purposes is accomplished similarly as for NH₃ by steam distg. an aq. soln. made alk. with KOH into a known quantity of standard H_2SO_4 . F. applied the method to the analysis of the salts and derivs. described above and states that, using the same precautions, the method is more exact than the analogous detn. of NH₃. *Physical properties of B*. B is a liquid with a weak, slightly unpleasant odor. At temps. near 0° it has a tendency to remain in superfusion. If crystn. is induced by seeding, the supercooled liquid solidifies gradually, forming large, monoclinic prisms, m. 16°. S. and S. (*loc. cit.*), working with a product of doubtful purity, found b. 275° and d_{4}^{20} 1.016. F., however, finds the pure compd. to have the following consts.; b_{10} 157°, b_{14} 279°, d_{4}^{20} 1.003, d_{4}^{25} 0.998, n_{D}^{20} 1.566, n_{D}^{25} 1.562. *Chem. properties of B and the description of its principal derivs.* Like NH₃ and A, B reacts with acids by simple addition. It does not form addition compds. with H_2O , alc., CS₂, phenols, etc. The *hydrofluoride*, obtained by treating B with an excess of aq. HF, forms cryst. masses, difficultly sol. in hot or cold H_2O and alc. Heated, it dissociates into its constituents without melting. The *hydrochloride*, prep'd. by double decompn. between a soln. of the sesquisulfate acidified with HCl and BaCl₂, fine needles, m. 198°, slightly sol. in cold H_2O , very sol. in boiling

H_2O , sol. in hot or cold alc. and in CHCl_3 and insol. in Et_2O . The *hydrobromide*, obtained similarly to the preceding salt, but without the corresponding acidification, crystallizes in fine needles, m. 184° , very sol. in H_2O acidified with HBr , sol. in alc. and CHCl_3 and slightly in Et_2O . The *hydroiodide*, made by the analogous method, forms long needles, m. 176° , very sol. in acidulated hot or cold H_2O , sol. in alc. and CHCl_3 but less in Et_2O . Open air evapn. of alc. solns. of the sesquisulfate yielded on cooling the neutral sulfate (Q), fine, quadrangular needles, m. 188° , slightly sol. in Et_2O and sol. in alc. H_2O decompns. it. The *sesquisulfate* (R) is conveniently prepnd. by treating B with half its wt. of $66^\circ \text{ H}_2\text{SO}_4$ and adding sufficient H_2O to bring the whole into soln. at 100° . On cooling, R is deposited in rounded cryst. masses, m. 197° , sol. in hot and cold H_2O with hydrolysis, sol. in alc. (15% at 73°) and nearly insol. in Et_2O . By dissolving R on the H_2O bath in 15 parts by wt. of dil. H_2SO_4 (1:10), and cooling, the *bisulfate* was obtained, elongated lanellae, m. 132° . Heated above its m. p., it decompns. at about 170° . Double decompn. between R and $\text{Ba}(\text{NO}_3)_2$ gives the *nitrate*, fine needles, very sol. in H_2O and alc. and slightly sol. in Et_2O . Heated, it m. 150° , assumes a greenish color, then violet, and deflagrates violently. The nitrate decompns. slowly when exposed to the air, but much more rapidly when kept in a closed vessel. Evapn. of a soln. of B in a large excess of H_3PO_4 furnished the *monobasic phosphate*, cryst. masses, m. 175° , slightly sol. in cold H_2O and sol. in alc.; hot H_2O hydrolyzes it. The *oxalate*, obtained by the direct action of $(\text{CO}_2\text{H})_2$ on B, forms colorless needles, m. 186° , not very sol. in H_2O but very sol. in hot alc. The *picate*, prepnd. analogously, crystallizes in yellow prisms, m. 164° , sparingly sol. in cold H_2O , hydrolyzed by hot H_2O and readily sol. in hot alc. The action of KCNO on R in alc. yields the unsym. *phenylcyclohexylurea*, needles, m. 221° , difficultly sol. in H_2O , sol. in alc. and Et_2O . *Ethylcyclohexyluniline*, from Et_2Br and B, is a slightly yellow, oily liquid, d₄ 0.999, b₁₀ 163° , b₂₀ 288° , insol. in H_2O , sol. in org. solvents and in dil. acids. Nascent HNO_2 and R in alc. at 0° give *phenylcyclohexylnitrosamine*, long, pale yellow needles, m. 37° , slightly sol. in H_2O and in MeOH and EtOH but very sol. in cold CHCl_3 and ligroin, not reduced in alc. by Zn powder and glacial AcOH . *Cyclohexylacetanilide*, obtained by the usual method employing Ac_2O , forms very small, brilliant crystals, m. 66° , insol. in cold H_2O , slightly sol. in hot H_2O , very sol. in alc., Et_2O and CHCl_3 . COCl_2 reacted energetically with B but the expected substituted urea could not be isolated from the product. BzCl and B produced a mixt. of the HCl salt and *phenylcyclohexylbenzamide*, prisms, m. 102° , b₂₀ 243° (decompn.); insol. in H_2O but sol. in alc., Et_2O , CHCl_3 and C_6H_6 . Diazonium salts and the organomagnesium compds. were without action on B. Heating B near its b. p. decompns. it into $\text{Pb}_2\text{NH}_2\text{H}$ and tarry substances. Concent. or fuming H_2SO_4 acts on B as it does on A, transforming it into $(\text{NH}_4)_2\text{SO}_4$. B and some of its salts are unstable when exposed to air and light. Color reactions given by B with various acids and their mixts. are described. A mixt. of HNO_3 , H_2SO_4 and H_2O in ratios of 1:10:9, resp., gives a beautiful orange-red color with B which serves to characterize it.

A. T. FRASCATI

The terpene series. ANORÉ DUBOSC. *Rev. prod. chim.* 24, 461-4 (1921).—A review, largely historical, of the chemistry and constitution of the terpenes. A. P.-C.

Unsaturation and molecular compound formation. II. O. MAASS AND J. RUSSELL. McGill Univ. *J. Am. Chem. Soc.* 43, 1227-30 (1921); cf. *C. A.* 12, 2470.—Pure $\text{Mc}:\text{CH}$ has been prepnd., and it has been shown that, unlike $\text{CH}:\text{CH}$, this substance forms a mol. compnd. with HBr . At higher temps. it combines with HBr to form an at. compnd.

H. JARMAIN CREIGHTON

Color and chemical constitution. XI. A systematic study of the brominated phenolphthaleins regarding the relation between position and color. JAMES MOIR. *Trans. Roy. Soc. S. Africa* 9, 129-36 (1921); cf. *C. A.* 15, 1712.—The general formula

previously derived (*C. A.* 15, 1712) reduces, in the case of bromophenolphthaleins, to the form $\lambda = 554 + 7.091(m + 0.091m^2)$, m being the number of *o*-Br atoms; in the case of *m*-Br atoms, m is to be doubled. Exptl. data for 5 mono-, 5 di-, 3 tri-, 2 tetra-, 3 penta-, 4 hexa-, and one heptabromophenolphthalein are shown to be usually within one unit of the values calcd. from the above formula, together with additive coeffs. which are given for substituents to which it does not apply. New monochloro- ($\lambda = 564$) and monoiodo- ($\lambda = 568.5$) phenolphthaleins derived from the *m*-halogenated phenols were also examd. The negative effect of the *p*-substituent previously noted in the case of benzaurine derivs. is not observed in the phenolphthalein series, and it is therefore suggested that the usual formulas for phenolphthalein and also fluorescein in alk. soln. require such amendment as will make them wholly phenolic in character, and not contg. the $-\text{CO}_2\text{Na}$ grouping. J. C. S.

Phenolcoumarein and resorcinolcoumarein. SRI KRISHNA. East London College, *J. Chem. Soc.* 119, 1420-5(1921).—*Phenolcoumarein* (A), $\text{C}_{11}\text{H}_{12}\text{O}_4$, is formed by heating 15 g. coumarin and 20 g. PhOH with 10 g. ZnCl_2 in a stream of dry HCl for 2 hrs., and then 2 hrs. without the HCl , pouring the black mass into 500 cc. 5% HCl, removing the ZnCl_2 and PhOH by boiling, and purifying the product by pptn. from NaOH with dil. HCl or AcOH and finally from Na_2CO_3 and then crystn. from dil. HCl; orange cryst. powder with 1 H_2O , which darkens and m. 103-5°. The alk. soln. is a pinkish red, changing to pale yellow on addition of HCl. *Potassium salt*, $\text{C}_{11}\text{H}_{12}\text{O}_4\text{K}_4\text{H}_2\text{O}$, pink powder. *Silver salt*, brown ppt. *Trimethyl ether*, from an alk. soln. of A and Me_3SO_4 in MeOH , pale gray powder. *Tribenzoyle derivative*, small, pale gray crystals, m. 154°. *Diacetate*, by heating 5 g. A, 10 cc. Ac_2O and 5 g. AcONa 4 hrs., brownish red ppt., m. 132°. *Tetrabromo derivative*, $\text{C}_{11}\text{H}_4\text{O}_4\text{Br}_4$, by heating 3.2 g. A and 3.2 g. Br in glacial AcOII for 2 hrs., brown powder. *Phenoldibromocoumarein*, $\text{C}_{11}\text{H}_4\text{O}_4\text{Br}_2$, by heating 10 g. coumarin dihydroide, 8 g. PhOH and 5 g. ZnCl_2 at 105° for 4 hrs. in a stream of HCl , brownish red powder, giving pink color with alkalies. *Resorcinolcoumarein*, $\text{C}_{11}\text{H}_{10}\text{O}_4$, from 14.6 g. coumarin, 22 g. *m*- $\text{C}_6\text{H}_4(\text{OH})_2$, and 10 g. ZnCl_2 as above, orange-yellow powder, containing 1 mol. H_2O , m. 176-7°. The AcOH soln. fluoresces slightly. *Tetrabromo derivative*, pale red powder, which shows no fluorescence in any solvent examd. C. J. W. str.

Influence of steric factors on intramolecular condensation. JAMES KENNER AND ERNEST WITHAM. Univ. Sheffield. *J. Chem. Soc.* 119, 1452-61(1921).—Reactions which involve the mobility of substituents in the *o*-position to a NO_2 group are comparatively free from the steric influences usually exerted by NO_2 groups. The effect of introducing a 2nd NO_2 or other *m*-derivative group in the *o*-position is to increase the reactivity of the mobile substituent. K. has proposed that this point is adequately explained by the view that the actual displacement of the mobile substituent is consequent on an intramol. condensation of the preliminary compd. formed through the agency of the NO_2 group with the reagent employed. An attempt has been made to furnish other examples which show that steric influences do not retard intramol. condensations to an extent comparable with their effects on intermol. reactions. *3-Chloro-o-tolunitrile*, $\text{C}_6\text{H}_5\text{MeCICN}$, long, slender prisms, m. 82-3°, b_{10}^{20} 143°. *3-Chloro-o-toluamide*, from the nitrile by heating with H_2SO_4 1.5 hrs., at 100-10°, scales, m. 167°. *3-Chloro-o-toluic acid*, by the careful addition of NaNO_2 to a hot soln. of the amide, long, slender needles, m. 102°. *3-Chloro-2-cyanobenzyl chloride*, by chlorination of the nitrile at 200°, yellow plates, m. 96°; it has marked lachrymatory properties. Upon condensing 3.95 g. of the chloride in 10 cc. alc. with $\text{AcCH}_2\text{NaCO}_2\text{Et}$ (3.1 g. ester and 0.5 g. Na in 10 cc. alc.), 1.2 g. *ethyl α,α-bis-3-chloro-2-cyanobenzylacetooacetate*, $[\text{Cl}(\text{CN})\text{C}_6\text{H}_3\text{CH}_2]_2\text{C}\text{AcCO}_2\text{Et}$, lustrous plates, m. 137°, were obtained together with 1.7 g. *ethyl 7-chloro-1-iminohydridene-2-carboxylate*, $\text{CIC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CO}_2\text{Et})\text{C:NH}$, prismatic need-

les, m. 64°. The cyclic structure was established by conversion with 10% H_2SO_4 into *7-chloro-1-hydrindone*, C_8H_7OCl , transparent prisms, m. 98°. *Semicarbazone*, needles from alc., m. 245° (decompn.). *m-Chlorobenzyl chloride*, prep'd. by the action of Cl on *m-MeC₆H₄Cl* at the h. p., hrs. 213-4°. *Ethyl m-chlorobenzylmalonate*, in 30-g. yield from 49 g. chloride and 49 g. $CH_3(CO_2Et)_2$, hrs. 213-4°. *Ethyl di-m-chlorobenzylmalonate*, hrs. 280°. *m-Chlorobenzylmalonic acid*, plates from C_8H_6 , m. 98-9°, with conversion into *8-m-chlorophenylpropionic acid*, prisms, m. 73-4°. *Anilide*, silky needles, m. 86-7°. *Chloride*, hrs. 161°. *5-Chloro-1-hydrindone*, prisms, m. 96-7°. *Semicarbazone*, small needles from alc. m. 242°. *Oxime*, elongated plates from dil. alc., m. 148°. *Isonitroso derivative*, fine needles, m. 232° (decompn.). C. J. West

9,10-Dihydrophenanthrene. HERBERT HENSTOCK. Shrewsbury. *J. Chem. Soc.* 119, 1461-3 (1921).—9,10-Dihydrophenanthrene (*C. A.* 2, 267) is conveniently prep'd. as follows: 25 g. $C_{10}H_{10}$ in 500 cc. hot glacial AcOH containing 25 g. fused $AcONa$ were slowly treated with 22.5 g. Br in 1500 cc. of the same solvent at room temp. After 2 hrs., the whole was poured into 5 l. H_2O , and after drying, the crude product crystd. from dil. alc. Yield, 95%. It forms transparent, flat triangles, which belong to the hexagonal system (rhombohedral, hemihedral, trigonal prisms with the face (001) strongly developed). If, in the above, 2 mols. Br are used, 9-acetoxyfluorene is a by-product; this is insol. in cold light petroleum; final purification was effected by heating 3 hrs. on a H_2O bath with $CrO_3\cdot AcOH$ and crystg. from C_6H_6 , thin needles, m. 272°. C. J. W.

Problems in the improvement of hydrocarbons. RUOOLF KORTSCHAU. *Z. angew. Chem.* 34, Aufsatzeil, 403 (1921).—K. reviews the most interesting and important new methods which have appeared recently, especially during the years 1920 and 1921, for the conversion of various types of hydrocarbons into more valuable com. substances: e. g., the production of tetralin and decalin from $C_{10}H_{16}$; the production of isoprene from C_6H_6 and Na acetone; the oxidation of paraffin to fatty acids; new methods for refining petroleum oils, etc.

ROGER ADAMS

Derivatives of anthraquinonediimide. LEON PIERRE GEORGE KEFFLER. Univ. Liverpool. *J. Chem. Soc.* 119, 1476-82 (1921); cf. *C. A.* 12, 140.—*6-Bromo-3,4-methylenedioxybenzonitrile* (*Gazz. chim. Ital.* 25, II, 188) is conveniently prep'd. by boiling 50 g. piperonaldoxime with 400 g. Ac_2O for 2 hrs., and decompn. with dil. HCl; needles, m. 135° (not 106°). *6-Nitro derivative*, by the action of 10 parts HNO_3 (d. 1.41) on piperonylonitrile (A) for 3 hrs. at room temp., long, yellow needles from alc., m. 144-5°. The H_2SO_4 soln. is emerald-green, turning to brown. *2,3,6,7-Dimethylenetetraoxy-anthraquinonediimide* (*C. A.* 12, 140) is obtained in 30% yield by gradually adding 10 cc. C_15O_2H to 10 g. A in 30 cc. $CHCl_3$; after the reaction has cooled to room temps. 50 cc. AcOH and 100 cc. Et_2O are added and the orange solid is crystd. from alc.- $PhNO_2$ and then from C_6H_6N , needles, m. 268°. *Dinitro derivative*, yellow, boat-shaped microcrystals from C_6H_6N , decomps. above 310°. The concd. H_2SO_4 soln. is orange. *6-Nitroratronitrile*, yellow needles, m. 165°. *2,3,6,7-Tetramethoxyanthraquinone-diimide*, $(MeO)_2C_6H_3 : [C(NH)]_2 : C_6H_2(OMe)_2$, prep'd. as above in 26% yield, slender needles from C_6H_6N , m. 265°. Mol. wt. detn. confirms the dimeric formulation. The imide is decompd. by heating with concd. HCl in a sealed tube at 150°. It does not react with Me_2SO_4 and is stable towards hot $KMnO_4$. *Dinitro derivative*, spear-head-shaped yellow microcrystals, m. 306°. The concd. H_2SO_4 soln. is reddish brown. The NO_2 groups are probahly in positions 3 or 6. *3-Methoxy-4-ethoxybenzonitrile*, prep'd. by the action of 15.6 g. EtI and 5 g. KOH on 14 g. vanilloniitrile, m. 102°. *6-Nitro derivative*, needles, m. 194°. *2,6-Dimethoxy-3,7-diethoxyanthraquinonediimide*, slender, long needles, m. 206°, from C_6H_6N . *Dinitro derivative*, yellow cubes from C_6H_6N , m. 295°. C. J. West

Some new sulfonic derivatives of oxindole and isatin. J. MARTINET AND O. DORNIER. *Compt. rend.* 172, 1415-7(1921).—In nitrating $\text{PhCH}_2\text{CO}_2\text{H}$ the NO_2 group occupies chiefly the *p*-position, and as the *o*-deriv. is the one desired, the yield is very poor. M. and D. sulfonated $\text{PhCH}_2\text{CO}_2\text{H}$, the SO_3H group going in the *p*-position and then nitrated it, forming $2,4-\text{O}_2\text{N}(\text{HO}_2\text{S})\text{C}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$ (**A**) (Ger. pat. 230028). Method.—Heat on the water bath one hour 13.5 g. $\text{PhCH}_2\text{CO}_2\text{H}$ and 70 g. 66° Be H_2SO_4 . The obtained mass is thrown into brine and in 24 hrs. an abundant yield of granular crystals of the water-sol. Na salt of **A** is pptd. Several crystns. produce a white compd. The Ag salt is insol. and darkens rapidly on exposure to light. **A** has one replaceable H and can be titrated with phenolphthalein as indicator. The NO_2 can be reduced to NH_2 by Zn or Fe in AcOH or $\text{Na}_2\text{S}_2\text{O}_4$. A hot soln. of **A** is treated with $\text{Na}_2\text{S}_2\text{O}_4$ and on concn. and refrigerating the oxindole-*β*-sulfonic acid (**B**) is pptd. in little rods and in small plates. M. and D. converted the **B** into isatin-*β*-sulfonic acid (**C**) which it is interesting to compare with the 5-isomer (*Compt. rend.* 172, 233). **C** treated with HNO_2 gives an isonitroso deriv., isatoxime-*β*-sulfonic acid (**D**), which differs from the 5-isomer in that **D** forms an intense purple with Zn or in aq. soln. SnCl_2 reduces **D** to the corresponding aminooxindole (**E**) which occurs as the chlorostannic compd. in small H_2O -insol. crystals. **E** is oxidized with $(\text{AcO})_2\text{Cu}$, Cu , HgO or FeCl_3 to isatin-*β*-sulfonic acid (**F**). Conc'd. $(\text{AcO})_2\text{Cu}$ is added to **E** suspended in boiling H_2O ; the soln. turns a bright red and finally yellow. The CuO ppts. and **F** is salted out with KCl as the K salt. Bayer also observed this fugitive red color but it has not been explained. This salt, $\text{C}_11\text{H}_4\text{O}_3\text{HSO}_4\text{K.H}_2\text{O}$, is sol. in H_2O , and gives the indophenol reaction. The Ba salt crystallizes with one mol H_2O . Its monobasic salts when treated with alkali change to violet and then to yellow. The indole ring is broken, forming alk. sulfoisatates. The yellow needles of the di-Ba salt crystallize with 1 H_2O . The dibasic salts of the 5- and 6-sulfonic acid derivs. close the ring under the influence of mineral acids, slowly in the cold and more rapidly in the hot. The K salt of **F** condenses with indoxyl in AcOH, forming an indirubin less deep in color than that made from the 5- SO_3H isomer. It has been also formed by condensing in dil. EtOIF **B** with isatin- α -anilide and forms a color that dyes animal fibers violet. Garnet crystals of the di-Na salt of isoindigo-*β,β*-disulfonic acid are obtained by condensing in water, containing a trace of H_2SO_4 , the Na salt of oxindole sulfonic acid with isatin-*β*-sulfonic acid.

R. E. SABIN

2-Phenyl-5-chloromethylloxazolidine. MAX BERGMANN, FRITZ RADT AND ERWIN BRAND. Kaiser-Wilhelm-Inst. f. Faserstoff-Chem., Berlin-Dahlem. *Ber.* 54B, 1645-52 (1921).—2-Phenyl-5-hydroxymethylloxazolidine having proved useful for the synthesis of mixed glycerides (*C. A.* 15, 3277), it seemed desirable to prepare the corresponding 5-halomethyl derivs. for further work along this line. Accordingly, 10 g. of the $\text{AcCH}_2\text{CO}_2\text{Et}$ compd. of $\text{CICH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$ (Schiff, *Gazz. chim. Ital.* 21, 11, 4 (1891)) was shaken with 20 cc. of 2.5 N HCl , in which it quickly dissolved with sepn. of $\text{AcCH}_2\text{CO}_2\text{Et}$, which was extd. with Et_2O after 0.5 hr. and the Et_2O removed by warming a short time; 4.8 g. BzH and a slight excess of solid K_2CO_3 were then added; on shaking the BzH quickly reacted with const. evolution of CO_2 and after 0.5 hr. yielded 80% of *2-phenyl-5-chloromethylloxazolidine* (**A**), long needles from CCl_4 -petr. ether, m. 82-3°; 4 g. treated with 2.8 g. BzCl and 1.6 g. $\text{C}_6\text{H}_5\text{N}$ in the usual way in CHCl_3 and after 24 hrs. shaken 0.5 hr. with 30 cc. of 5 N HCl and evapd. *in vacuo* gave 79% *γ-chloro-β-hydroxypropylbenzamide*, pptd. from AcOEt or Me_2CO by petr. ether in 6-sided tables, m. 107-8°, sol. in H_2O with neutral reaction to litmus. With *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{COCl}$ instead of BzCl the authors succeeded in isolating the intermediate product, *2-phenyl-3-p-nitrobenzoyl-5-chloromethylloxazolidine*, prisms or tables, m. 120-2°, which, when shaken with HCl , yielded the *γ-chloro-β-hydroxypropyl-p-nitrobenzamide*,

long needles from C_4H_6 , m. 110-2°. These acylations, yielding products with the acyl group on the N, show that A must have a substitutable H on the N and can therefore have only the oxazolidine structure $CICH_2CH(CH_3)NH.CHPH_2O$ and not that of a Schiff

base. When 12.3 g. A is added to 4 g. KOH in 50 cc. of 96% alc. at 15-20°, allowed to stand 24 hrs., filtered from the KCl, concd. *in vacuo*, decompd. with H_2O and extd. with Et_2O there are obtained 6.8 g. *benzalephhydrinamine* (B), $PhCH_2NCH_2CH_2CH_2O$,

$b_{1-1} 102-4^\circ$, and a small amt. of *2-phenyl-5-ethoxymethylloxazolidine*, b. 25° higher; the amt. of the latter is somewhat greater when NaOEt is used instead of alc. KOH. B (6 g.) allowed to stand 24 hrs. with 100 cc. of alc. satd. at 0° with NH_3 , evapd. to a sirup, treated with HCl (whereby much BzH is split off), evapd. *in vacuo* and allowed to stand *in vacuo* over P_2O_5 yields *B,B'-diaminoisopropyl alcohol hydrochloride*, hygroscopic prisms, m. about 175-7°; picrate, yellow prisms, m. 240-1° (decompn.) (Goe-deckemeyer, *Ber.*, 21, 2690(1888), gives 230°); *oxalate*, obtained directly from B by splitting off the BzH, after the NH_3 treatment, with $(CO_2H)_2$, extg. with Et_2O and adding alc. to the aq. layer, lancet-shaped leaves, m. 215°, sol. in H_2O with neutral reaction to litmus. As shown in the earlier paper, $CH_2:CHCH_2NHBz$ (C) (which has now been obtained, after long standing in cold winter weather, as a radiating cryst. mass, m. 17°) gives on chlorination, in considerable amt., $CICH_2CH(OBz)CH_2NH_2$ (D). When 5.5 g. C in 12 cc. moist $CHCl_3$ in ice is treated with a slow current of Cl until a slight excess remains even on standing and is then treated with Et_2O and washed several times with H_2O , the $Et_2O-CHCl_3$ layer on evapn. below 25° yields 5.6 g. *B,y-dichloro-propylbenzamide*, long needles from AcOEt and low boiling petr. ether, sinters 99°, m. 100-1°, while the aq. layer on evapn. *in vacuo* gives 2.1 g. of the *hydrochloride* of D, needles from a little AcOH with 1 drop concd. HCl and much Et_2O , relatively easily sol. in cold H_2O , which when treated in hot soln. with a few drops concd. HCl crystallize in 6-sided prisms more difficultly sol. in cold H_2O ; both forms m. 191°; 6 g. rubbed with 10 cc. cold H_2O and slowly treated with the calcd. amt. of N KOH yields 4.9 g. $CICH_2CH(OH)CH_2NHBz$, identical with the benzoylation product of A, whose easy formation from a compd. of the type D is easily understood in the light of all recent observations on the migration of acyl radicals, while its formation from the isomeric compd. $BzOCH_2CH_2ClCH_2NH_2$, involving the migration of Bz, HO and Cl, would be hard to explain. This indicates that in the rearrangement of dihalogen derivs. of compds. of the type C only the halogen on the middle C atom is involved and the products really have structures of the type D and not of the isomeric type $BzOCH_2CH_2ClCH_2NH_2$.

CHAS. A. ROUILLER

Comparison of some isomeric isocyanines. FRANCES MARY HAMER. Univ. Cambridge. *J. Chem. Soc.* 119, 1432-44(1921).—This work was undertaken with the object of comparing the photographic sensitizing action of a series of isomers. *6-Nitroquinaldine* (*Monatsh.*, 24, 87) m. 164°, not 174°. *Methiodide*, $C_{11}H_{10}O_2N_2I$, green crystals, m. 214° (decompn.). *6-Nitroquinaldine methiodide*, orange crystals, m. about 245°. *5-Aminoquinaldine*, dried at 105°, m. 117-8°. *6-Aminoquinaldine*, m. 187-5°. *7-Aminocoumarine* m. 93.5-4°, not 183° (*J. prakt. Chem.* 48, 170(1893)), or at 73.5°, with H_2O of crystn. *Cinnamylamino* derivs. were prep'd. by treating a $CHCl_3$ soln. of the base with the Cl, then shaking with N NaOH and crystg. from alc. The MeI derivs. were prep'd. by heating with 10% excess MeI in a sealed tube at 100° for 24-48 hrs. *5-Cinnamylaminoquinaldine*, highly refractive, pale yellow prisms, m. 257°. *Methiodide*, minute yellow crystals, which turn orange on becoming anhydrous, m. 228-34°. *6-Cinnamyl derivative*, almost colorless crystals, m. 256.5°. *Methiodide*, fine yellow needles, m. 269°. *7-Cinnamyl derivative*, yellow crystals, m. 128.5-

9.5°; *methiodide*, yellow, m. 280°. *5-Cinnamylaminoquinoline*, small yellow crystals, m. 250°; *methiodide*, yellow, m. 238°. *6-Cinnamyl derivative*, m. 184° to a pale yellow fluid, which then crystd. and m. 199°; these may be *cis*- and *trans*-forms of the base; *methiodide*, yellow, which changes to orange at 110°, and back to yellow at 170°, m. 274°. *7-Cinnamyl derivative*, m. 202°. *Methiodide*, yellow needles, m. 280° (decompn.). The Ac derivs. were prep'd. by boiling with 2 times the theory of Ac₂O for 15 min., dilg. with H₂O and pptg. with NH₄OH. *5-Acetylaminoquinoline*, m. 204.5°; *methiodide*, orange, m. 250-60°. *6-Acetyl derivative*, m. 168.5°; *methiodide*, pale yellow, decompns. about 254°. *7-Acetyl derivative*, m. 194°; *methiodide*, orange or yellow, m. 267°. *5-Acetylaminoquinoline methiodide*, bright yellow, m. 250-4°. *6-Acetylaminoquinoline methiodide*, yellow, m. 317°. *7-Acetylaminoquinoline*, m. 167.5°; *methiodide*, yellow prisms, m. 295-310°. Methiodides of the 8-derivs. could not be obtained. *1,1'-Dimethylisocyanine iodide*, C₁₁H₁₄N₂I, prep'd. by heating 5.78 g. quinoline-MeI and 2.85 g. quinoline-MeI in 100 cc. alc. with 0.27 g. Na in 30 cc. alc. for 15 min., lustrous, green needles from MeOH, m. 268° (decompn.). It is a powerful sensitizer. For moderate exposures the sensitization extends to 5500, and there are 2 max. at 5850 and 5350. The crests of the absorption bands lie at 5550 and 5200. The NO₂ derivs. could not be condensed with the unsubstituted derivs. *5-Cinnamylamino derivative*, minute, purple crystals, with a green metallic luster on being crushed, m. 200-30°; this is the feeblest sensitizer prep'd. The sensitization extends to 6100. *6-Cinnamylamino derivative*, compact, purple crystals, with golden luster, m. 280-4°. This gives a very clean plate and is by far the most powerful sensitizer of this group. The band reaches to 6500 and there is a max. at 6000, which is more intense than that in the green at 5500. *7-Cinnamylamino derivative*, minute purple crystals with brassy luster, decomp. about 250°. This is a weak sensitizer. *6'-Cinnamylamino derivative*, reddish purple substance with brassy iridescence, m. 247°. The limit of sensitization is at 6300. *7'-Cinnamylamino derivative*, dull purple crystals (very low yield), m. 200°. It is a poor sensitizer. *5-Acetylamino derivative*, small, brown crystals, or larger needles with green or steel-blue iridescence, m. 240-60°. It is inferior to the parent substance as a sensitizer. *6-Acetylamino derivative*, green and gold prisms or compact bronze crystals, m. 268° (decompn.). *7-Acetylamino derivative*, minute purple crystals with brilliant green luster, m. 280-90°. It is a good sensitizer. *6'-Acetylamino derivative*, large compact crystals with green metallic reflex, m. 310° (decompn.). *7'-Acetylamino derivative*, olive-green crystals with greenish yellow luster, decomp. 250-80°. On hydrolysis of the acetylamino derivs. the amino derivs. may be obtained. *5-Amino derivative*, small purple crystals with green luster, m. 250-5° (decompn.). *6-Amino derivative*, compact, dark, green crystals, or bright green with golden iridescence, m. 266-71°. *7-Amino derivative*, small green crystals, or prisms with Cu-like appearance, m. 250°. *6'-Amino derivative*, small, green, brilliantly iridescent prisms, m. 266-71°. *7'-Amino derivative*, purple ppt., which, boiled with MeOH, changed to green and gold pleochroic crystals, m. 259-60°. The limit for these compds. is between 6600 and 6700. From these series it is evident that the magnitude of the influence on the sensitizing action exerted by a given substituent varies largely according to the situation of the group. When the H in position 5 has been replaced, the extension of the sensitizing band into the red is at a minimum. With each of the isocyanines the α -sensitizing max. is situated 200-350 tenth meters nearer the red end of the spectrum than is the corresponding absorption band. In the sensitizing curves it is found that this crest in the cases of the 6-, 7-, and 6'-substituted isocyanine lies nearer the red than does that in the equiv. 5- and 7'-substituted dyes.

C. J. WEST

* Derivatives of some *o*-nitro ketones. II. S. GABRIEL AND WILH. GERHARD. Univ. Berlin. *Ber.* 54B, 1613-8 (1921); cf. *C. A.* 15, 3471.—*o*-Nitrodibenzoylacet-

EORG. Physiol. Department, Aberdeen Univ. *Biochem. J.* 15, 498-506(1921); cf. *C. A.* 13, 2925.—The activity of trypsin as measured by its digestive action on fibrin and on caseinogen has been shown to be affected to such a different degree by alcohol that one of two conclusions must be drawn: either that two enzymes are concerned in the action, or else that the two substrates are acted on by different groups or side chains. Treatment of trypsin solns. with HCl at high or low temps. shows that the power to digest fibrin is more readily destroyed than the power to digest caseinogen. Freshly prepared aq. extracts of pancreas generally do not coagulate milk, but are very active proteolytic agents, both on fibrin and caseinogen. The milk-coagulating power of pancreatic extracts is more easily destroyed by heat than the proteolytic power.

BENJAMIN HARROW

Studies of gelatin. I. The dynamics of the formation of gelatin from ossein. A. B. MANNING AND S. B. SCHRYVER. Imp. Coll. Techn., London. *Biochem. J.* 15, 523-529(1921).—The middle portions of the femurs of oxen about two years old were used. Five grades of bone (based on passage of particles through meshes of various sizes) were decalcified with 3 per cent cold HCl. The rate of extraction of gelatin from decalcified bones of various graded sizes was measured at 100° and 90°. The extraction curves for the larger sized particles are similar to the curves for autocatalytic reactions, though the process of extraction is not autocatalytic. The rate of extn. increases with the finer division of the bones. Owing to the high porosity of the bone there is the same surface available, whatever the size of the particles. The different behavior must be attributed to the time taken for the adsorbed substance to diffuse along the pores and so arrive at the surface.

BENJAMIN HARROW

Enzymes of the abdominal adipose tissue of the common turkey, *Meleagris gallopavo*. J. S. HEPBURN. Hahnemann Medical College, Philadelphia. *J. Am. Chem. Soc.* 43, 1963-5(1921).—Study was made of the abdominal adipose tissue (crude gizzard fat) of 6 hen turkeys of known history. Catalase, lipase (acting on tributyrin), and esterase (acting on Et butyrate) were always present. Simple reductase and oxidase acting upon phenolphthalein were usually present. Oxidases, acting upon α -naphthol and upon tricresol, and protease were not found. Aldehyde reductase and peroxidases were present in several of the samples.

JOSEPH S. HEPBURN

The structure of thymus nucleic acid and its possible bearing on the structure of plant nucleic acid. P. A. LEVENE. Rockefeller Inst. *J. Biol. Chem.* 48, 119-25 (1921).—L. does not consider that the new expts. described by Jones (*C. A.* 14, 2489) are sufficient evidence to prove the ether linking of the nucleotides in yeast nucleic acid. That the H-ion concn. of the reacting medium does not change when yeast nucleic acid is hydrolyzed by a pancreatic enzyme might well be due to the fact that nucleic acid as a polyphosphoric acid possesses considerable buffer effect and that each liberated nucleotide is a comparatively weak acid and does not markedly affect the H-ion concn. of the buffer. The fact that the rate of hydrolysis of nucleic acid is identical with that of a mixt. of the four nucleotides indicates that the union between individual nucleotides is more labile than that between the phosphoric acid and the carbohydrate in each nucleotide and makes it self-evident that the first step in the hydrolysis is the formation of the 4 nucleotides and that the further progress of hydrolysis is the same as of 4 nucleotides. This ready formation of 4 nucleotides is consistent with the theory of the ester linkage of the nucleotides of L. rather than with Jones' theory of ether linkage. L. has reinvestigated the question of the occurrence of a dinucleotide among the products of the hydrolysis of thymus nucleic acid and by the methods employed was able to isolate only diphosphoric acid nucleotides. "It is possible that the monophosphoric acid nucleotides are secondary products and that the hypothetical dinucleotide (Levene and Jacobs, *C. A.* 6, 3428) is only a mixt. of mononucleotides. Thus for the present,

until the existence of the dinucleotide is definitely proved, the structure of the thymus nucleic acid should be expressed in analogy with that of the yeast nucleic acid," i. e., in ester form, the phosphoric acid on-one nucleotide combining with the carbohydrate of the other.

A. P. LOTHROP

Preparation and analysis of animal nucleic acid. P. A. LEVENE. Rockefeller Inst. *J. Biol. Chem.* **48**, 177-83(1921).—The method of prep. animal nucleic acid has been improved and the substance has been obtained from the spleen, pancreas and liver as follows: Free the fresh tissue from fat and mince. Take up 2,500 g. of the minced tissue in 3,000 cc. of H_2O , add 300 g. of NaCl and keep the mixt. boiling for 4 hrs. with a steam coil. Add 80 g. of AcONa and 60 cc. of 33% NaOH soln. and allow the mixt. to stand overnight. Neutralize with AcOH and add picric acid as long as a ppt. forms. Filter and to the filtrate add HCl until the mixt. turns slightly opalescent. Ppt. the nucleic acid by adding 10% $CuCl_2$ soln. Filter and convert the Cu salt into the free acid by treatment with 5% HCl. Repeat the treatment once. Dissolve the free nucleic acid in 5% NaOH soln., acidify with AcOH and ppt. with 95% alc. containing 4% of HCl. Wash with 95% alc. until the washings no longer show the presence of Cl ions. Wash with abs. alc. and E_6O and dry. The substance should not show the presence of even traces of biuret-giving material and should give a negative test with orcein. For the analysis of the purine bases alcoholysis is preferable to hydrolysis. If the nucleic acid is suspended in MeOH and HCl gas is passed through the soln., the nucleic acid dissolves rapidly and the purine bases soon begin to sep. as HCl salts. The sepn. is practically complete in 2 hrs. The cleavage is brought about by the heat developed by the absorption of the HCl gas. None of the samples prepd. from liver, spleen and pancreas showed the presence of pentose and all contained the 2 purine bases, adenine and guanine. The yield of the bases was smaller from the pancreas and liver nucleic acids. There was considerable deviation from the theory required for the compn. of a hexosetetrancleotide in the case of the liver nucleic acid which requires explanation as does also the fact that the pancreas nucleic acid gave less purine bases than that from spleen although it differs little from it in elementary compn. Further work on these problems is in progress. A. P. LOTHROP

The liver lecithin. P. A. LEVENE AND H. S. SIMMS. Rockefeller Inst. *J. Biol. Chem.* **48**, 185-96(1921); cf. *C. A.* **14**, 3616.—Liver lecithin contains two satd. fatty acids, palmitic and stearic and two unsatd. acids one of which on reduction is converted into stearic acid and the other into arachidic acid. The exact degree of unsatn. of either one of the two acids is not as yet known but there is evidence which indicates that the one yielding arachidic acid is tetra-unsatd. as on the addition of Br it yields a substance which analyzed for an octobromide of arachidic acid. From mol. wt. detsns. of the hydrooleithin obtained by Paal's method from liver lecithin it is evident that liver lecithin consists of a mixt. of monoleithins. *Prepn. of pure free lecithin from its $CdCl_2$ salt.* By an improved method the analytically pure substance can be obtained in good yield; about 50 g. from 100 g. of the $CdCl_2$ salt. Dissolve 100 g. of the $CdCl_2$ salt in 300 cc. of warm $CHCl_3$ and pour the soln. slowly with rapid stirring into 400 cc. of MeOH containing 20 g. of NH_3 gas. Allow to stand for a short time then filter off the ppt. through a folded filter paper. Concentrate at a low temp. under diminished pressure. Filter off any ppt. of fat which may settle out. Dissolve the remaining lecithin in 5-10 cc. of glacial AcOH, pour the soln. into 800 cc. of boiling hot Me_2CO , stir and allow to cool to room temp. Decant or filter the supernatant liquid to free it from a very small (1-2 g.) dark ppt. which settles out. Cool in a freezing mixt. to -5° and decant if a second small ppt. settles out. Concentrate under diminished pressure until all the Me_2CO and most of the AcOH are removed. Add H_2O a little at a time and shake or stir until a thick emulsion of a light brown color is obtained. Pour this into 800-1,000 cc. of

Me_2CO chilled to -5° . Stir carefully and allow to stand overnight at 0 to -5° . Transfer to a crystg. dish and wash free from excess H_2O with cold dry Me_2CO . Decant the Me_2CO and dry the lecithin in a vacuum desiccator.

A. P. LOTHROP

Conductivity and permeability. W. J. V. OSRRHOUT. Harvard Univ. *J. Gen. Physiol.* 4, 1-9(1921).—*Laminaria* was used in these expts. When an elec. current passes from a salt soln. into an animal or vegetable cell, ions must enter the cell; under such conditions, therefore, the elec. resistance of the protoplasm may be regarded as a measure of its permeability to ions. The elec. current flows partly through the cell wall and partly through the protoplasm of the cell. The relative amts. of these 2 portions of the current can be calcd. by means of a formula. (Cf. *C. A.* 10, 2744; 15, 540.) Such calcns. show that conclusions derived from studies of the resistance of the tissue as a whole can also be applied to the resistance of cell protoplasm and hence to its permeability to ions.

CHAS. H. RICHARDSON

Comparative hydrolysis of gelatin by pepsin, trypsin, acid and alkali. JOHN H. NORTHROP. Rockefeller Inst. *J. Gen. Physiol.* 4, 57-71(1921).—Purified gelatin in 5% soln. was used in these expts. It was hydrolyzed to various stages by one of the hydrolyzing agents after which pepsin or trypsin was added and the increase in hydrolysis noted. The reaction was followed by a modified formol titration method. (Cf. Northrop, *C. A.* 15, 3833.) The peptide linkages of the gelatin mol. which are most rapidly split by pepsin or trypsin are more resistant to acid hydrolysis. Linkages hydrolyzed by pepsin are also hydrolyzed by trypsin, but trypsin hydrolyzes some linkages not attacked by pepsin. Those linkages must be rapidly hydrolyzed by pepsin but are slowly attacked by trypsin. Those linkages attacked by both enzymes are among those most rapidly hydrolyzed by alkali. Thus the course of the early stages of the hydrolysis of gelatin is similar with pepsin, trypsin, and alkali but is quite different with acid.

CHAS. H. RICHARDSON

Characterization of amylases. Preliminary communication. H. v. EULER AND OLAF SVANBERG. *Z. physiol. Chem.* 112, 193-230(1920).—Malt diastase was used. It was prepd. by extg. malt with distd. water for 1.5 days and dialyzing the filtrate. The soln. employed contained 0.14% of solids. With quantities of this soln. varying between 0.1 cc. and 2.0 cc., 25 cc. of 2% starch soln. and 10 cc. of a phosphate mixt. of $p_H=5.6$, the velocity of the hydrolysis (measured by the amt. of maltose produced), rose proportionally to the enzyme concn. By keeping the enzyme concn. const. it was proportional to the amt. of starch. Variations in the quantity of phosphate were without effect. NaCl and K salts influenced the velocity only slightly. The optimum H^+ concn. was found to be at $p_H=5.6$. E. and S. suggest a formula, the use of which would permit a direct comparison between the degrees of activity of different amylase prepns. It is $Sf = K \times g.$ maltose/g. of enzyme, where Sf is the sugar-producing power per g. of dry weight and K is the velocity const. calcd. according to the monomol. formula. The value Sf has been calcd. from some of the data already in the literature.

R. L. STEHLE

The course of the reaction between arginine and arginase. R. E. GROSE. *Z. physiol. Chem.* 112, 236-51(1920).—Decreasing velocity consts. were observed for the reaction. When ornithine was added to the reacting mixt. the extent of hydrolysis of the arginine was less than the 70-85% usually observed. Urea had little inhibiting influence and leads G. to believe that something else than a condition of ordinary equil. is involved. The expts. were carried out at a p_H of 6.62 and the formol titration method was used.

R. L. STEHLE

Proteolytic enzymes in normal and pathological urine. S. G. HEDIN. *Z. physiol. Chem.* 112, 252-81(1920).—Normal and pathological urines were investigated for their content of enzymes acting upon (1) casein at $p_H=8$, (2) Witte's peptone at $p_H=8$,

and (3) casein at $p_H = 1.6$. In normal urine the first is absent or present in small amt. but in the urine collected during the fever stage of croupous pneumonia it is decidedly increased. The hydrolysis of Witte's peptone in alk. soln. is demonstrable in normal urine and is increased in the fever stage of pneumonia, and in leucemia but in the latter there is no decided increase in the action on casein at $p_H = 8$. There was no regularity of increase in the action on casein at $p_H = 1.6$. R. L. STIGLEZ

The preparation of highly active saccharases. V. The P content of purified saccharase solutions after thorough dialysis, and the microdetermination of phosphorus. H. v. EULER AND O. SVANBERG. *Z. physiol. Chem.* 112, 282-94(1920); cf. *C. A.* 15, 1730.—A saccharase prep., was obtained from yeast which contained 0.10% of org. P which was not in the form of a carbohydrate-phosphoric acid combination. Carbohydrate corresponding to 90% of the dry weight and 1.27% N were also present. These figures are the basis for speculation concerning the nature of saccharase. R. L. S.

Action of emulsin on galactose. M. BRIDEL. *J. pharm. chim.* 24, 209-18(1921); *Pharm. J.* 107, 250(1921).—See *C. A.* 15, 2457. S. WALDBOTT

The application of the hydrogen electrode (KOLTHOFF) 2.

B—METHODS AND APPARATUS

STANLEY E. BENEDICT

Method of protein removal from body fluids for the purpose of simultaneous determination of many constituents. GRNKO MUKAI. Imp. Univ., Kiushiyu, Japan. *Biochem. J.* 15, 516-20(1921).—Method: 4 cc. serum (if whole blood or urine is used, dil. with distilled water until the concn. of proteins becomes 0.3 per cent) is measured into a beaker containing about 80 cc. distd. water, and neutralized to litmus paper with dil. AcOH. The fluid is heated quickly over a small flame just to boiling. During heating, stir the fluid gently, 10 cc. of acid NaOAc (prepd. by adding AcOII to a hot 20% NaOAc soln. until it becomes acid to alizarin red) is added and the boiling continued for about 30 seconds, so as to produce a visible coagulum. Transfer to a 100-cc. flask and make up to the mark with water. Shake, pour back into the original beaker, and add 3 g. talcum powder (which removes the last traces of protein from soln.). Stir the soln. for 5-10 min., warm on water bath up to 40-45°, and mix well. After cooling, add 2 to 3 g. talcum, mix the soln. and filter. Use the filtrate for the detn. of the various constituents of serum. Control expts. show that the method is applicable for the detn. of non-protein nitrogen and chlorides in blood serum, etc. B. H.

Sensitization of the Trendelenberg frog preparation for the measurement of adrenaline. T. ALDAY-RGDONNET. *Biochem. Z.* 110, 306-18(1920); *Physiol. Abstracts* 6, 71-2(1921).—The Trendelenberg prep. of frog muscle has certain advantages over the mammalian blood pressure method when small amts. of adrenaline are used, but is less accurate than the latter method. The frog muscle is rendered more sensitive by addition of more Ca to the perfusion liquid, the muscle apparently having been injured during perfusion by a disturbance of the equil. between Ca and K. J. S. H.

Van Deen's reaction and hydrocyanic acid. LUCIANO P. J. PALET. *Anal. soc. quim. Argentina* 6, 508-12(1918).—Experimental proof is given that HCN, contrary to Selmi's statement (*Accad. Sci. Bologna*, 1879), does not interfere with Van Deen's reaction; on the other hand, KCN prevents the production of the blue color given by the reagent (H_2O_2 and tincture of guaiacum resin) in presence of fresh blood. This is shown to be due to the alkalinity of ordinary cyanide, as a positive reaction is obtained after neutralization of the free alkali with acetic acid. Selmi's negative results must be attributed to the alkalinity of the cyanide used. J. C. S.

The estimation of chlorides in whole blood. JOHN B. RUGGER. Detroit. *J. Lab. Clin. Med.* 6, 44-5(1920).—The method is an application of the Volhard titration

to the protein-free filtrate obtained by the Folin system of blood analysis. Acidify a 10% soln. of Na tungstate with an equal vol. of HNO_3 , filter off the lemon-yellow ppt. and to the filtrate add a few drops of AgNO_3 test soln. Any turbidity which may be seen by transmitted light indicates an appreciable chloride content. To purify, pour the tungstate soln. into an equal vol. of 50% H_2SO_4 , let settle, and siphon off the supernatant fluid or suck off through a Buchner funnel. Wash by decantation until the test for chlorides is no longer given; dissolve in the requisite amt. of 40% NaOH (7 cc. for each 10 g. of Na tungstate taken, and make neutral to litmus; add water to make a soln. of d. 1.15 and filter. The following solns. are required. (1) Standard AgNO_3 soln.: AgNO_3 crystals 7.2653 g., HNO_3 , sp. gr. 1.42, 250 cc., satd. soln. iron-ammonium-alum 50 cc., distd. water to 1000 cc. (2) NH_4SCN soln.: 0.75 g. in 1000 cc., to be adjusted by titration so that 25 cc. equals 5 cc. of the Ag soln. (3) soln. of $\text{Na}_2(\text{CO}_3)$: 1 g. to 100 cc. One cc. of the soln. is evapd. to dryness in a 1-oz. salt mouth bottle. The oxalate forms a thin film over the bottom and is sufficient for 10-15 cc. of blood. (4) Cl-free, neutral 10% Na tungstate soln., sp. gr. 1.15. (5) $\frac{1}{4} N \text{ H}_2\text{SO}_4$: To 1 vol. of Na tungstate soln. in a suitable flask, add 1 vol. oxalated blood and 1 vol. $\frac{1}{3} N \text{ H}_2\text{SO}_4$. Agitate and allow to stand for an hour or longer, preferably in an ice-box. Dil. to 10 vols., agitate and filter. The filtrate should be water-white, and give no ppt. with an equal vol. of HNO_3 (absence of tungstate). The presence of tungstate greatly obscures the endpoint in the succeeding titration. To 20 cc. of the filtrate, representing 2 cc. of whole blood, in a 50-cc. volumetric flask, add 10 cc. distd. water and 10 cc. of the standard Ag soln. Dil. to the mark, shake vigorously to coagulate the AgCl , and centrifuge or filter. Titrate 25 cc. of the filtrate with NH_4SCN to the appearance of the first brown tinge. This is sharp. The number of cc. of the cyanate soln. is subtracted from 25 and the difference multiplied by 50 to obtain the number of mg. of NaCl per 100 cc. of whole blood.

E. R. LONG

A study of the catalase reaction. SERGIUS MORGULIS. Univ. Neh. *J. Biol. Chem.* 47, 341-75(1921); cf. *C. A.* 14, 3182.—"The use of very large quantities of H_2O_2 (equiv. to 500 or 600 cc. of O_2), as is practiced commonly in researches on catalase, is objectionable because the depressing effect is great unless very large amts. of the catalase prepns. are employed. There is no obvious advantage in working with such tremendous quantities. On the other hand, when an attempt is made to compare the catalase activity of prepns. of presumably different strengths, the depressing effect will be much greater in the case of the weaker sample and under such conditions the tendency will be to exaggerate the differences. In fact the entire method of comparing several samples of catalase on the basis of the amt. of O_2 which they respectively liberate from H_2O_2 is of questionable accuracy. The comparison should instead be made between respective quantities of catalase prepns. required to set free the same amt. of O_2 from a given quantity of H_2O_2 . It is further advisable to adjust the reaction to follow some definite course (a 75% decompr. of the H_2O_2 is a very good basis). Although the O_2 formation is a linear function of the quantity of catalase, this rule does not hold true when either the catalase or the H_2O_2 is in great excess. When, however, the catalase is varied to produce a certain degree of decompr. with the same quantity of H_2O_2 , the catalase strengths will be inversely proportional to the quantities used for the tests. The method of estg. the catalase strength followed in most investigations on catalase is so crude and untenable from a chem. standpoint that one naturally is reluctant to accept the conclusions drawn from those researches, especially where the conclusions are of far-reaching significance. Another important matter is the fact that in the catalase expts. the reaction is allowed to go on for a set length of time, usually 10 or 15 min. The reasons for detg. relative reaction speeds from the time periods required to effect a given result, rather than from the results effected in a given time period have

been fully discussed by Osterhout (*Science* **48**, 172(1918).) It should be noted, however, that when the reaction is permitted to run for 10 min., only 50 or perhaps 60% of the reaction is completed. For comparative purposes, it may be argued, this will not matter, and this might be true if the reaction were always brought to the same end-point. This is not likely to be the case. If, on the other hand, the reaction is so vigorous and rapid as to be completed within the 10 to 15 min. it is practically certain that there is a great excess of catalase. In this event, of course, the O_2 evolution will again fail to give a correct measure of the relative catalase strengths inasmuch as there is no means of detg. whether or not the relative excess is the same in each instance. Little credence can therefore be given to results of catalase expts. unless very large differences are demonstrated." The liberation of O_2 from H_2O_2 is markedly affected by the reaction of the H_2O_2 ; the optimum H-ion concn. for the catalase reaction is $pH = 7$ but the reaction at $pH = 6.4$ is 98% complete so that expts. should be conducted in a medium slightly on the acid side ($pH = 6.7-6.9$) which is sufficient to prevent spontaneous decompr. of the H_2O_2 which occurs most readily at $pH = 7.0$ and above. The soln. should be brought to the definite pH by adding 0.01 N NaOH rather than by the use of phosphate buffer mixts. The depressing effect of a large excess of H_2O_2 on the liberation of O_2 is due to the fact that the reaction is a reversible one; the max. evolution of O_2 occurs when the amt. of H_2O_2 used is such that 65-70% of the total amt. of H_2O_2 available is decompl. The catalase reaction has been generally regarded as belonging to the monomol. order, only one substance, H_2O_2 , undergoing decompr. This, however, is not the case as not only does the H_2O_2 disappear but the catalase as well is used up and there is a definite quant. relation between the interacting catalase and the H_2O_2 . When 95-100% of the available O_2 is liberated, the reaction is unquestionably monomol.; if the decompr. is between 85-95% the reaction follows the curve of a 1½ mol.; between 70-80% the reaction runs true to the bimol. course and below 65% the actual amt. of O_2 set free as well as the reaction velocity are considerably diminished. As the reaction follows almost ideally the bimol. curve with a decompr. of H_2O_2 of about 75-80%, it is a simple matter to so adjust conditions that the results of an entire exptl. series can be made really comparable.

A. P. LOTHROP

Vital staining. WERNER SCHULEMANN. *Z. angew. Chem.* **34**, Aufsatzteil, 237-0 (1921)—Acid dyes injected into an animal are distributed and excreted more rapidly the smaller their mols., the less they tend to form mol. aggregates, and the less changes in temp., ageing of solns. and the addition of electrolytes tend to depress ionization and favor aggregation. Acid dyes in the ionized condition seem to penetrate all cells, but accumulate only in such as are able to cause aggregation and flocculation of the dye. It is hoped that such studies will lead to methods that will make it possible to study the distribution and accumulation of foodstuffs and drugs in cells. T. G. PHILLIPS

C—BACTERIOLOGY

A. K. BALLS

Remarks on the alkalinity of nutrient bouillon and nutrient medium as well as determination of it by titration with the use of indicators. JOSEF REITSTÖRTER. Vienna, *Z. Hyg. Infektionskrankh.* **90**, 218-26(1920).—A review of the theories of indicators and the influence of various "buffers" such as phosphates and proteins in maintaining a const. H-ion concn. In titrating media the necessity of taking into account the influence of the buffers present is emphasized. F. A. CAJORI

Experiments on the action of hydrocyanic acid on bacteria. E. TEICHMANN AND W. NAGEL. Univ. Frankfurt. *Z. Hyg. Infektionskrankh.* **90**, 401-16(1920).—An investigation of the most favorable conditions for the destruction of bacteria by HCN gas. The action of HCN is more effective with an increase in temp., a low moisture

content and in the presence of strong light. It is found "that a const. HCN concn. of 2.25 to 2.5% (by vol.) at a temp. of 24 to 28° in an atm. of 15 to 20% satd. in dissembled light will kill in 24 hrs. *Staphylococcus aureus* and *B. coli* if they are present on a dry substratum."

F. A. CAJORI

Hydrogen-ion concentration and titratable acidity in relation to bacteriological media. I. L. BALDWIN. *Proc. Indiana Acad. Sci.* 1919, 171-3.—The concn. of H ions and not total amt. of acid present affects the bacterial growth; consequently a method which measures the former is preferable to one which measures titratable acidity. Another serious error in the detn. of the reaction of media by the old method of titrating with the standard soln. lies in the buffer effect of the ingredients of the media. A number of samples of media were prepd. according to the Am. Public Health Assoc. standards and the reactions detd. by both methods; the results are tabulated and show that the method of making media + 1 to phenolphthalein can not be depended upon to bring it to neutrality and that in the case of all careful work the reaction must be detd. by measurement of the H-ion concn.

N. A. LANGE

Bacteria in sugar-cane products (CHURCH) 28.

D—BOTANY

CARL L. ALSBERG

The presence of loroglossin, glucoside of "Loroglossum hircinum," in different species of indigenous orchids. P. DELAUNEY. *Bull. soc. chim. biol.* 3, 238-46(1921); cf. *C. A.* 15, 546, 2202.—The same glucoside has been extd. from *Orchis simia*, *O. bifolia*, *Ophrys aranifera* and *apifera*, and *Cephalanthera grandiflora*. A. T. CAMERON

The oxalic acid content of young spring leaves and some remarks on this acid. ARMINIUS BAU. *Z. tech. Biol.* 8, 151-5(1921).—By pptg. oxalic acid with Ca acetate, the presence of oxalic acid to the amount of .05 to .5% can be demonstrated in exts. of young leaves. Gmelein-Kraut then is in error in stating that there is a lack of "oxalation" in young spring leaves. F. A. CAJORI

Recent advances in science—Plant physiology. J. H. PRIESTLEY. Univ. Leeds. *Sci. Progress* 16, 201-7(1921).—Review of recent work on proteins and their relation to electrolytes and to H-ion concn. JOSEPH S. HEPBURN

Acerin. The globulin of the maple seed (*Acer saccharinum*). R. J. ANDERSON. N. Y. Agr. Expt. Sta. *J. Biol. Chem.* 48, 23-31(1921).—"The principal protein of the seed of the silver maple (*Acer saccharinum*) has been isolated and purified. This protein, for which the name *acerin* is proposed, is a globulin. It could not be obtained in cryst. form but sepd. on dialysis in small uniform globular particles." The purified acerin is a nearly white heavy powder which on combustion leaves no weighable ash. A number of different preps. were made and all of these preps. showed close agreement on analysis. The av. compn. of acerin is as follows: C 51.44 H 6.8, N 18.34, S 0.55, O 22.87%. When analyzed by the Van Slyke method it was found to contain the following % of basic amino acids: cystine 0.55, histidine 1.43, arginine 10.07, lysine 1.07." It is very similar in compn. and N distribution to arachin the globulin from the peanut but the % of the basic amino acids differs in the two globulins.

A. P. LOTHROP

The respiration of leaves in a vacuum or in an atmosphere poor in oxygen. L. MAGUENNE AND E. DEMOUSSY. *Compt. rend.* 173, 373-7(1921).—Leaves of aucuba or pear left in tubes *in vacuo* or in the presence of small amts. of air and in water free from air and aerated. Aucuba leaves darken on death in the absence of O, pear leaves darken on death only when O is present. In the absence of O and light leaves die in 3-4 days. Small amts. of O allow the leaves to live longer, the time depending on the relative amts. of O and leaf tissue. In vacuum and diffuse light leaves

of aucuba may live as long as 3 months, owing to the O liberated by photosynthesis. At the end of the expt. the leaves were tested by their ability to decompose CO₂. In H₂O kept satd. with air leaves live in the dark for several weeks. For the species studied normal respiration in the presence of O is necessary to support life. Intramolecular respiration can support life for only a short time. The authors conclude that normal respiration is able to liberate CO₂ from substances not available for intramolecular respiration. The two types of respiration do not have a common origin. They are entirely separate functions not only in their mechanism but also in the effect they have on the life of green plants.

T. G. PHILLIPS

The presence of a glucoside decomposed by emulsin in two species of the genus *Melampyrum*. MARC BRINEL AND MARIE BRARCKE. *Compt. rend.* 173, 414-6 (1921).—By the biochem. method of Bourquelot (cf. *C. A.* 13, 1486) on exts. of *M. arvense* and *M. pratense* the presence of glucosides hydrolyzed by emulsin was proved. A black ppt. is formed during the action of emulsin. It is probable that the glucoside is aucubin, but further work is needed to make the identification complete. T. G. PHILLIPS

Free anthocyanidins in the flowers and red leaves of certain plants. ST. JONESCO. *Compt. rend.* 173, 426-9 (1921).—Free anthocyanidins were obtained from flowers of *Pelargonium* and *Papaver rhoes* and from the red or olive-green leaves of *Prunus pissardi* by extg. with AmOH the residue from the extn. of anthocyanins with acids (cf. *C. A.* 15, 2903). The presence of anthocyanins, anthocyanidins and pseudo bases together indicates their close interrelationship and their relation to the disappearance of the red color in plants. T. G. PHILLIPS

The saponarin in *Mnium cuspidatum*. ANTOINE KOZLOWSKI. *Compt. rend.* 173, 429-31 (1921).—A substance was found dissolved in the cell sap of the leaves of this moss, which gives a blue to rose color with iodine, and is supposed to be a saponarin. Acids make the blue color more intense, and alkalies change it to yellow. T. G. PHILLIPS

Mobile starch and geotropism. E. ZAEPPPEL. *Compt. rend.* 173, 442-5 (1921).—Mobile starch grains or "statoliths" fall to the lower side of the cells containing them. These cells also contain reducing sugars and amylase. Owing to the relatively slow diffusion of sugars their concn. is greater near the starch grains from which they are being formed by the action of amylase, that is at the lower side of the cell. Thus a difference in osmotic pressure arises between the upper and lower parts of the cell and this causes the bending in response to gravity. T. G. PHILLIPS

The occurrence of calcium oxalate in the gidgee wattle (*Acacia cambagei*). THOS. STEEL. *Proc. Linnean Soc. N. S. Wales* 46, 256-8 (1921).—The timber and bark of *A. cambagei* contained the following percents of CaC₂O₄H₂O in the dry wt.: outer bark, 18.82; inner bark, 18.82; outer wood, 5.81; inner wood, 3.81. Of the barks of six other species of *Acacia*, none contained more than 9% CaC₂O₄H₂O. S. considers the CaC₂O₄ a waste product, since that in the outer bark could not be used again by the tree. T. G. PHILLIPS

Eucalyptus oil glands. M. B. WELCH. *J. Proc. Roy. Soc. N. S. Wales* 54, 208-17 (1920).—Mostly anatomical. The oil is present in the form of a fine emulsion. In different species this emulsion is broken by varying concns. of EtOH. The protective colloid is probably protein. T. G. PHILLIPS

Mucilaginous substances of *Laminaria*. MM. GRUZBWSKA. *Compt. rend.* 173, 52-4 (1921).—Several methods for extg. the mucilaginous substances from *Laminaria* are given. The rotatory power of an alk. soln. of the mucilage of a concn. 0.752 in 100 is $[\alpha]_D = -150.4$. In the mucilage of *Laminaria flexicaulis* there are at least 2 substances, one of which is sol. in the presence of salts. The mucilage may be completely hydrolyzed by successive treatments, in some cases 8 or 9 being required. Thus 1.9 g. per 100 cc. heated 4 to 5 hrs. on a boiling water bath gave 1.475 g. of sugar calcd. as

glucose. After the removal of the sugar the remainder was dissolved in 0.5% Na_2CO_3 , acidified with 5% HCl and again heated on the water bath 4 to 5 hrs. when 0.125 g. of sugar was obtained. A third treatment gave 0.04, the 4th 0.025, the 5th 0.0335 and the 6th 0.0135, total 1.7 g. The sugars sepd. were identified by their osazones as glucose and galactose.

L. W. RIGGS

Distribution of iron in plants. L. MAQUENNE AND R. CERIGHELLI. *Compt. rend.* 173, 273-8(1921).—Iron was detd. in various parts of 11 trees or shrubs, 8 green vegetables, 8 seeds and 3 stone fruits. In the trees and green vegetables the leaves and buds contained from 3 to 10 times as much Fe as the young wood freed from bark. With the exception of the thorn bush, young leaves contained several times as much Fe as old leaves. The Fe content of centrifuged juice of green vegetables was reduced to one third or much less by boiling. The embryo of seeds generally contained more than one half of the Fe, the cotyledons less and the teguments least. In the apricot, cherry and prune the kernel contained more Fe than the shell. In general, Fe in vegetable tissues moves toward the organs of active life and of reproduction. (Cf. following abstract.) Also in *Bull. soc. chim.* 29, 899-905(1921).

L. W. RIGGS

General presence of manganese in the vegetable kingdom. GABRIEL BERTRAND AND MME. M. ROSENBLATT. *Compt. rend.* 173, 333-6(1921); cf. preceding abstract.—Mn was detd. in the tissues of 15 different plants, consisting of 10 green vegetables, one weed, wheat bran and 3 pulpy fruits. Sep. detns. were generally made on different parts of each plant and Mn was found in every case. In the various parts of orange, citron, and manderin the Mn content ranged from 0.21 to 0.71 mg. per 100 g. of dry matter. Roots of shepherd's purse gave the highest Mn content of any plant tissue tested, the figure being 17.6 mg. per 100 g. of dry matter. Vegetables averaged 3 to 4 mg. and wheat bran 3.9 mg. Also in *Bull. soc. chim.* 29, 910-15(1921). L. W. RIGGS

The chemical constituents of green plants. XII. The volatile constituents of oak leaves. H. FRANZEN. *Z. physiol. Chem.* 112, 301-16(1920); cf. *C. A.* 15, 2110.—The acids, aldehydes and alcs. detected in the leaves of *Quercus sessiliflora* were practically the same as those observed in similar analysis of hornbeam and chestnut leaves.

R. L. STURTEVANT

E—NUTRITION

PHILIP B. HAWK

NORMAL

The metabolism of a European in the tropics. WILHELM CASPARI AND CLAUS SCHILLING. Berlin. *Z. Hyg. Infektionskrankh.* 91, 57-132(1920); cf. *C. A.* 15, 1153.—The metabolism of two individuals was followed in great detail during a resting and work period in Berlin and during similar periods after they had gone to the west coast of Africa. The diets in Berlin and Africa were nearly identical, both in caloric and N content and in the kinds of foods eaten. It was found that protein and fat are equally well utilized in both climates, that the N balance is maintained in Africa as easily as under similar dietary conditions in Berlin despite the greater N loss in the perspiration in the hotter climate. The body uses food in the tropics as efficiently as elsewhere. No change in body temp. or pulse rate was noted. Similar results were found in an expt. with a European who had dwelt in the tropics long enough to have become acclimated. F. A. C.

Antiscorbutic properties of concentrated fruit juices. IV. ARTHUR HARNIEN AND ROBERT ROBISON. *Biochem. J.* 15, 521-2(1921); cf. *C. A.* 13, 2067; 14, 2015.—The earlier investigation has shown that orange juice can be evapd. to a dry residue without suffering any loss of vitamine C, even after standing for two years,—provided the material be kept in a dry atmosphere and at room temp. The present expts. show that if stored at a temp. of 29°, the juice is much more rapidly destroyed. B. H.

Formation of vitamine A in living plant tissues. K. H. COWARD AND J. C. DRUMMOND. Univ. Coll., London. *Biochem. J.* 15, 530-9(1921).—For the methods for testing, see Drummond and Coward (*C. A.* 15, 252). Seeds such as carrot, turnip, cabbage, cress, peas and white and yellow maize were fed to rats in known amounts daily, in addition to a basal diet deficient in vitamine A. The results confirm McCollum's opinion (*The Newer Knowledge of Nutrition*, 1918) that the majority of these tissues are deficient in vitamine A. Germination of seeds, which has been shown to increase vitamine C, does not affect vitamine A. Etiolated seedlings, grown in sand, do not contain vitamine A, but green seedlings—obtained by growing in sand, watering with normal Sachs' soln., and exposing the seeds to light—such as the green shoots of turnip, maize and peas, possess a much higher value as a source of vitamine A than either the seeds from which they sprang, or the corresponding etiolated leaves. Water culture experiments with *Tradescantia* ("wandering jew"), using Sachs' soln. as a culture medium, seem to show that vitamine A can be synthesized by the green plant from inorganic material. Green cabbage leaves, unlike the white ones, contain appreciable quantities of vitamine A; 1.5 g. of the fresh material fed daily to rats induces "very fair growth." Using lower plants, the authors find that mushrooms induce but slight growth, whereas common green seaweeds found on the south coast of England (*Ulva* and *Cladophora* sp. ?) are "as potent as the green land plants such as cabbage." "Vitamine A in green leaves does not appear to be associated with proteins. It may be extracted in the fat removed by solvents and appears in that fraction of the fat which is resistant to saponification."

BENJAMIN HARROW

Researches on vitamine A. VII. Notes on the factors influencing the value of milk and butter as sources of vitamine A. J. C. DRUMMOND, K. H. COWARD AND A. F. WATSON. Univ. Coll., London. *Biochem. J.* 15, 540-52(1921); cf. *C. A.* 15, 1557.—For details as to method, see Drummond and Coward (*C. A.* 15, 252). Colostrum appears to be considerably richer in vitamine A than later milk, thereby suggesting a function of the former that has been quite overlooked by physiologists. Butter appears to be less potent as a source of vitamine A than the same amount of fat supplied in the original milk. The wide variations in vitamine A content shown by various samples of butter are largely due to differences in the diet of the cow. Processes used in butter-making, such as exposure to air at high temps., and the "renovation" of rancid butter, tend to reduce the content of vitamine A.

BENJAMIN HARROW

Feeding of infants and children. JULIUS LEVY. *Arch. Pediatrics* 38, 595-602 (1921).—A discussion of the diet of infants and young children. JOSEPH S. HEPBURN

The effect of cottonseed meal upon the growth and reproduction of cows. STANLEY COMBS AND R. S. CURTIS. N. C. Agr. Expt. Sta. *J. Dairy Sci.* 4, 334-41(1921).—Feeding expts. were conducted on 40 cows, with the use of cottonseed meal and hulls alone and with other ration. Cows were from six months to little over 1 yr. old. Those fed on meal and hulls died within 82-226 days after starting on the ration. Some of those fed on meal with other feeds died while others which were discontinued were sluggish and very much weakened. Results with older animals may have been far different. Present work is outlined and results with meal used with other feeding stuffs appear fairly satisfactory.

H. A. LEPPER

Dietary factors influencing calcium assimilation. I. The comparative influence of green and dried plant tissue, cabbage, orange juice, and cod-liver oil on calcium assimilation. E. B. HART, H. STEENBOCK AND C. A. HOPPERT. Univ. Wis. *J. Biol. Chem.* 48, 33-50(1921).—"Expts. with goats, milking and dry, show that there is something in fresh green oats as compared with dry oat straw which increases the amt. of Ca assimilated. The oat hay, dried out of direct sunlight, but in a fairly well-lighted attic, seemed to retain the properties of the fresh green oats studied. Orange juice

administered in generous quantities (120-240 cc. per day) had no consistent effect on Ca assimilation. Raw cabbage (1,000 g. per day) or dried cabbage had no effect on Ca assimilation. These data eliminate the antiscorbutic vitamine as a factor in Ca assimilation and conform with clinical experience in rickets. Cod-liver oil (5-10 cc. per day) consistently changed negative Ca balances to positive balances. The limited data show that the same factor affecting Ca assimilation and resident in green oats and grasses is present in cod-liver oil. Work with other types of animals and with food materials other than those used in these expts. is now in progress." A. P. LOTHROP

The antiscorbutic principle in the juice of the potato, extracted in the presence of acids. BEZSONOFF. *Compt. rend.* 173, 417-9(1921); cf. C. A. 15, 1746.—The loss of the antiscorbutic properties of raw potatoes during grinding was prevented by adding to 200 g. of the potatoes before grinding 5 g. of a mixt. of 1 part citric or tartaric acids and 4 parts of sucrose. The concn. of acid in the juice obtained is sufficient to prevent discoloring. It is thought that the antiscorbutic vitamine is destroyed by the oxidizing enzyme causing discoloring. T. G. PHILLIPS

The digestion of infant foods. T. SCHMIESING. *Z. physiol. Chem.* 112, 295-300 (1920).—Detsns. were made of the gastric secretion and absorption in dogs with intestinal fistulas after feeding whole milk, milk and gruel, buttermilk, woman's milk and "Keller's malt soup." Large differences were not noted in the amts. of secretion or in the time required to leave the stomach. R. L. STEHLE

F—PHYSIOLOGY

ANREW HUNTER

Influence of muscle plasma upon the width of the vessels in the muscles. M. G. SOULBERG. *Arch. néerland. physiol.* 4, 460-76(1920); *Physiol. Abstracts* 5, 430.—The hind legs of frogs were perfused by a modification of the Laewen-Trendelenberg method. Lactic acid in concns. ranging from 1 in 7000 to 1 in 10000 produced vasoconstriction. Protein-free plasma, prep'd. from either resting or fatigued thigh muscles, produced vasodilation. The muscle plasma contg. its proteins produced vasoconstriction followed by vasodilation. JOSEPH S. HEPBURN

Clinical and experimental studies on lactation at the University of Minnesota. LE ROY M. A. MAGORR. *Arch. Pediatrics* 38, 557-67(1921).—A summary of the work completed and published, and an outline of proposed studies. A bibliography is included. JOSEPH S. HEPBURN

Relation of uric acid excretion to hemorrhage of the portal region. G. KOLLMANN. *Wiener klin. Wochschr.* 70, 1967-9(1920); *Physiol. Abstracts* 5, 561(1921).—Proof was not obtained that the excretion of uric acid is dependent upon the vol. of blood in the vessels of the intestine. JOSEPH S. HEPBURN

Gas exchange and mechanical work of the frog heart. II. E. LÜSCHER. *Z. Biol.* 72, 107-28(1920); *Physiol. Abstracts* 6, 40-1(1921); cf. C. A. 14, 1139; 15, 2118.—When the heart contracts under after-load conditions, the consumption of O_2 increases with the degree of after-loading provided that the initial or diastolic pressure be low (100 mm. H_2O). The consumption remains const., or decreases slightly with the increase in after-load pressure, when the diastolic pressure is high (400 mm. H_2O). With an after-load pressure of 300 mm. H_2O , the consumption remains const. or decreases when the diastolic pressure increases from 80 to 300 mm. H_2O . The consumption during isotonic contractions increases with the increase in diastolic pressure. Since the consumption tends to the same max. in isotonic, isometric, and after-load contractions, a stimulus can produce the max. energy exchange under different mech. conditions, provided that a fixed relation exist between the surface and the vol. of the muscular elements at the commencement of contraction; otherwise the gas exchange

is decreased. The consumption of O_2 in after-load contraction is $8.6 \times 10^4 \times \text{vol.} \times \text{pressure}$. This equation probably also holds true for isometric contraction. The const. has a different value for each diastolic pressure in isotonic contraction. The effective work in after-loaded systole is 31% of the total work. JOSEPH S. HRPBURN

The potassium content of normal and some pathological human bloods. VICTOR C. MYERS AND JAMES J. SHORT. N. Y. Post-Graduate Med. School and Hosp. *J. Biol. Chem.* **48**, 83-92(1921).—The K content of whole blood and of serum has been detd.; especial care was taken to prevent hemolysis or the passage of any K from the cells since whole blood contains about 10 times as much K as the serum. More satisfactory results are obtained on serum than on plasma since hemolysis is more likely to occur when Na citrate or $(NH_4)_2CO_3$ has been added as anticoagulants. The K content of normal whole blood is rather less than 20 mg. per 100 cc. and for whole blood 8-12 times this amt., being roughly proportional to the total solid and red cell content. No increase in the K content of the serum was noted in the samples of blood obtained from 7 nephritis with marked N retention. These observations do not lend support to the suggestion of Smillie (*C. A.* **9**, 3091) that some of the symptoms of uremia may be due to a K poisoning as a result of K retention. In none of the pathol. cases examd. were abnormal amts. of K found when the serum was sepd. within 2 hrs. after the blood was drawn.

A. P. L.

Creatinine and creatine in muscle extracts. II. The influence of the reaction of the medium on the creatinine-creatinine balance in incubated extracts of muscle tissue of the albino rat. FREDERICK S. HAMMETT. Wistar Inst. *J. Biol. Chem.* **48**, 133-41 (1921); cf. *C. A.* **15**, 3862.—"When exts. of muscle tissue of the albino rat are incubated at body temp. for 24 hrs. there occurs an increase in the creatinine content, the relative degree of which depends in part upon the reaction of the incubated ext. When the ext. is allowed to develop its own reaction, which is slightly acid to rosolic acid, an increase of 100% takes place. When the ext. is buffered to neutrality by phosphate mixt. the increase is 175%, and when the ext. is made slightly alk. the increase is 124%. Since there is no change in the total creatinine content of these exts. this increase in creatinine must take place at the expense of the creatine present. Moreover, since the conditions of the expts. simulate to a considerable degree conditions in the living tissue in that the reactions took place in muscle ext. dild. with Tyrode's soln. it is probable that creatinine is formed from creatine in muscle tissue in the living organism. The apparent anomaly of an increased creatine excretion in conditions of exptl. acidosis and alkalosis is explicable in part on the basis of the retardation of creatinine formation from creatine when the reaction is slightly acid or alk. If similar effects are produced in the organism the continued production of creatine as a result of a phase of muscle metabolism would result in a relatively greater concn. of this in the blood and its excretion in larger amts. in the urine. It is probable that the transformation of creatine to creatinine in the muscle exts. is facilitated by an enzyme, but no evidence is afforded of the presence in such exts. of any 'creatinase' or 'creatase.' The only time when a destruction of creatinine or creatine takes place is when the exts. undergo putrefaction." A. P. LOTHROP

Studies of the thyroid apparatus. IV. The influence of parathyroid and thyroid tissue on the creatinine-creatinine balance in incubated extracts of muscle tissue of the albino rat. FREDERICK S. HAMMETT. Wistar Inst. *J. Biol. Chem.* **48**, 143-52(1921); cf. *C. A.* **15**, 3312—"Evidence is presented which demonstrates that the addition of parathyroid tissue to exts. of muscle tissue of albino rats retards the increase of creatinine formation normally taking place during incubation. This occurs in acid, neutral, or alk. mixts. The addition of thyroid tissue to similar exts. has no effect upon the creatinine formation that is demonstrable by the methods used. Since the max. retarda-

tion effect of the parathyroids occurs in solns. buffered to neutrality, while the max. creatinine formation takes place at the same reaction, the conclusion is justified that this parathyroid effect is an expression of a direct influence of the parathyroids on creatine metabolism. The exact role of these glands, or the phase of creatine metabolism in which the parathyroids exert their main activity is not yet clear. Speculation would be premature, particularly in view of the fact of the increased creatine production in the organism when the parathyroids have been removed. The clarification of these points awaits further experimentation."

A. P. LOTHROP

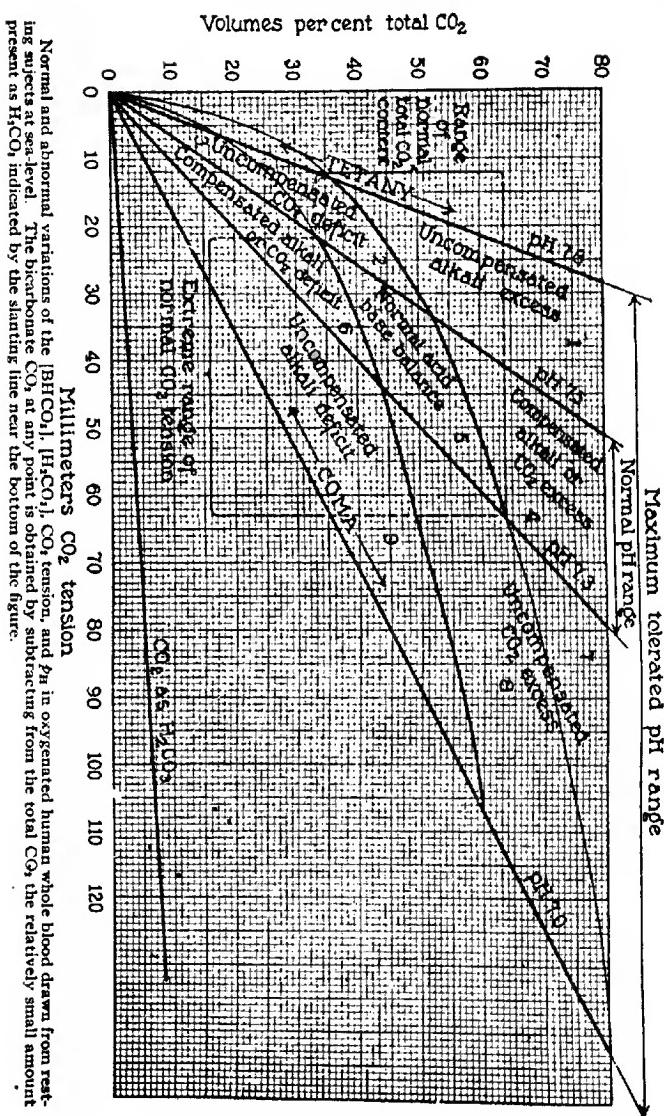
Studies of acidosis. XVII. The normal and abnormal variations in the acid-base balance of the blood. DONALD D. VAN SLYKE. Rockefeller Inst. *J. Biol. Chem.* 48, 153-76 (1921); cf. *C. A.* 14, 1689.—"The possible variations in the acid-base balance of the blood may be stated as follows: the blood bicarbonate may be high, low, or normal, and in each of these conditions the p_H may be high, low, or normal. There are thus classified 9 theoretical possible conditions. Only one of them is normal, that in which both bicarbonate and p_H are within normal limits." All the remaining 8 abnormal possibilities have now been produced experimentally and some of them occur clinically as well. The 9 possible conditions are represented by 9 areas in the fig. and are in order as follows: (1) uncompensated alkali excess; (2 and 3) uncompensated CO_2 deficit; (4) compensated alkali excess or CO_2 excess; (5) normal acid-base balance; (6) compensated alkali deficit or CO_2 deficit; (7 and 8) uncompensated CO_2 excess; (9) uncompensated alkali deficit. "In order to det. which one of the possible variations exists in the blood *in vivo* it is necessary to ascertain two of the involved variables, such as the p_H , $[\text{BH-CO}_2]$, and $[\text{H}_2\text{CO}_3]$. With any two of them a point can be located in its proper area on a diagram such as the fig. shown, but with any one of them alone it cannot be done. Under most conditions, pathological as well as normal, the p_H is kept normal. When this is the case detn. of either CO_2 tension or the bicarbonate in either plasma or whole blood suffices to indicate the condition. The plasma bicarbonate detn. by the gasometric method of Van Slyke and Cullen (*C. A.* 11, 2207) or the titration method of Van Slyke, Stillman, and Cullen (*C. A.* 13, 2058) is adequate for this case, and therefore suffices for the study of metabolic conditions (*e.g.*, those usually met in diabetes, nephritis, and metabolic disturbances of infants) in which the source of acid-base disturbance is retention of non-volatile acids, while the respiratory control of the blood reaction is unaffected. It is not adequate to cover conditions in which the respiratory control of the blood reaction is so disturbed that the p_H becomes abnormal as happens in anesthesia." The max. available alkali of the blood consists of the entire alkali of the bicarbonate plus that portion of the other buffer alkalies which is yielded when the p_H changes from normal (7.4) to the minimum (7.0) compatible with life. These amts. are as follows: 0.0205 M bicarbonate alkali (equiv. to 46 vols. % of bicarbonate CO_2 , of which $\frac{3}{4}$ and perhaps $\frac{1}{4}$ may be used for neutralization of acid without change in p_H , and the remainder if the p_H falls to 7.0; 0.0075 M alkali (equiv. to 17 vols. % of bicarbonate CO_2) from other buffers available only when the p_H falls to 7.0; of this 0.0075 M alkali the greater part is normally bound to hemoglobin. The original should be consulted for the theoretical discussion of the combined variations of blood bicarbonate and p_H and the conditions associated with them. An extensive bibliography is appended to the article.

A. P. LOTHROP

G—PATHOLOGY

H. GEOFON WELLS

Experiments with different tuberculins. D. SCHÜSSLER. Univ. Heidelberg. *Deut. med. Wochschr.* 46, 1102-4 (1920).—Cutaneous tuberculin reactions were made on tuberculous children with tuberculins from human tubercle bacilli of various manu-



Normal and abnormal variations of the $[\text{BHCO}_3]$, $[\text{HCO}_3^-]$, CO_2 tension, and p_{CO_2} in oxygenated human whole blood drawn from resting subjects at sea level. The bicarbonate CO_2 at any point is obtained by subtracting from the total CO_2 the relatively small amount present as H_2CO_3 indicated by the slanting line near the bottom of the figure.

factures and with tuberculins from bovine and turtle tubercle bacilli. There was no constant relation between the disease and a particular tuberculin. S. AMBERG

Blood sugar before and after the therapeutic reduction of the adrenal glands in convulsive patients according to Heinr. Fischer. W. BAUSCH. Univ. Giessen. *Deut. med. Wochschr.* 46, 1353(1920).—Removal of one adrenal gland in patients suffering from convulsions does not lead to pathological changes in the sugar content of the blood.

S. AMBERG

The own-urine reaction in tuberculosis of the lungs. E. BRESSEL. Univ. Rostock. *Deut. med. Wochschr.* 46, 1385(1920).—The reaction obtained with the urine of patients suffering with tuberculosis when injected intracutaneously in these patients after concur. was tested in 50 cases. It was compared with the reaction obtained with 1:10,000 tuberculin. The reaction occurs early. It is associated on the whole with spreading of the tuberculosis process. It is painful.

S. AMBERG

Fat antibodies. H. MÜCH. Univ. Hamburg. *Deut. med. Wochschr.* 47, 209-11 (1921).—Polemics.

S. AMBERG

The significance of acidity of the feces in dysentery for the bacteriological diagnosis of dysentery. FRITZ JACOBY. *Z. Hyg. Infektionskrankh.* 90, 1-21(1920).—From a study of the titratable acidity of the feces in dysentery J. points out that the acid reaction in dysentery is independent of the presence of the dysentery bacillus. This bacillus is very sensitive to acid which explains the greater ease of identification of this bacillus in specimens of fresh feces.

F. A. CAJORI

Experimental investigations on the etiology of rickets. FRITZ WAUSCHKUHN. Hyg. Inst. Univ. Königsberg. *Z. Hyg. Infektionskrankh.* 91, 242-59(1920).—Rats and dogs were exposed to dust-laden and infected air with no evidence that such conditions are conducive to the onset of rickets. Domestication or confinement of animals is in no way connected with the etiology of rickets.

F. A. CAJORI

The content of specific proteins in the blood serum. R. DOER AND W. BERGER. Univ. Basel. *Z. Hyg. Infektionskrankh.* 93, 147-62(1921).—Two sets of guinea pigs were sensitized by subcutaneous injection of mixts. of human serum and dog serum. For the first set normal serum was used. For the second set dog serum, that had been rendered immune to human serum, and human serum were used. The guinea pigs of the second set were killed by anaphylactic shock with 10 times smaller doses than those of the first set, that is the process of immunization raised the serum content of biologically active protein. By use of the refractive index the authors find in immune serum an increase of serum globulin and a decrease of serum albumin.

F. A. CAJORI

Bile salts in the blood in jaundice. A. GILBERT, E. CHABROL AND HENRI BÉNARD. *Compt. rend. soc. biol.* 83, 1602-5(1920).—A technic for the detection of the presence of bile salts is described; and results obtained by its use on the blood of patients are reported. Technic.—Two cc. of serum are mixed in a large test tube with 20 cc. of 95% alc. The tube is heated on the water bath until its contents begin to boil. The ppt. is collected on a filter; the filtrate is received in a porcelain capsule, and is then evapd. to dryness on a water bath. The residue is triturated in the capsule with 5 cc. of H_2SO_4 , previously dild. with its own vol. of water, and cooled. The resulting soln. is transferred to a test tube, and mixed with 1 drop of a 1% soln. of furfural. The tube is kept at a temp. of 60° for 5 min. If bile salts are present, the contents of the tube become a deep brown rather than a reddish purple; this abnormal color is attributed to the influence of other org. compds. present in serum. However, the color produced by bile salts is characterized by an absorption band, in the green portion of the spectrum in the region of 0.515 micron, with diffuse borders, which always blots out the spectrum to the right more or less, and extends toward the left when the other org. compds. were also present. By this procedure, bile salts may be detected if present in a concn. of

0.1 g. per l. The technic was used on the serum of a number of subjects with the following results. Twelve patients were free from jaundice; some were suffering from diseases of the liver, others were not; bile salts were not found in their sera. These salts likewise were not found in the sera of 4 patients suffering from chronic jaundice due to hypertrophy of the spleen, even when bile pigments were present in the blood in the ratio of 1 part in 6000. Bile salts were found in the sera of 14 patients who were suffering from jaundice; their blood contained more than 1 part of bile pigment in 3000; their urine was characterized by the presence of bile; these 14 patients were diagnosed as suffering from the following diseases: jaundice (cattarrhal, or syphilitic, or pneumonic, or due to salvarsan), biliary cirrhosis, neoplasms of the liver and the pancreas.

JOSEPH S. HEPBURN

Role of parathyroids and calcium metabolism in tetany. A. K. W. ARNTZENIAS. Univ. Leiden. *Dissertation* (1919); *Endocrinology* 3, 560-1 (1919).—Two patients suffered from postoperative tetany, and 2 others from severe diarrhoea associated with tetany. Three of the patients showed a negative Ca balance; administration daily of 4 g. of either CaCl₂ or Ca lactate decreased the symptoms of tetany and produced a marked improvement in the general condition of all 3 patients; however, the Ca metabolism was improved in but 1 of these patients. The fourth patient showed symptoms of latent tetany, but no disturbance of the Ca metabolism, and was also greatly benefitted by administration of Ca. The patients were also treated by administration of cow or sheep parathyroids, fresh or desiccated; as many as 100 glands were given in a single dose, but no improvement resulted. The conclusion is drawn that hypo function of the parathyroids changes the Ca metabolism, and thereby gives rise to tetany. The association of chronic diarrhoea and tetany is attributed to increased excretion of Ca as soaps in the feces, and to pluriglandular insufficiency. JOSEPH S. HEPBURN

Some features of arteriosclerosis. FRITZ C. ASKENSTEDT. *J. Am. Inst. Homeopathy* 14, 327-38 (1921).—The following data of chem. interest are reported. In the urine of 165 patients under 50 years of age, the av. ratio of urea to purine N was 90.4:1, of urea to NH₃ 31.79:1. In the urine of 133 patients 50 or more years of age, the av. ratio of urea to purine N was 83.1:1, of urea to NH₃ 30.8:1. All cases of pregnancy, diabetes, and acetouria were excluded. The ratios for NH₃ suggest a slightly greater tendency to acidosis in the aged. In patients over 50 years of age, the av. abs. amt. of purine N excreted daily in the urine was not increased in cases of high blood pressure above the value found in cases of low blood pressure. However, in 46 cases with a blood pressure below 150 mm. systolic tension (av. 130 mm.), the av. ratio of urea to purine N was 85.4:1, while it was 82:1 in 51 cases with a blood pressure of 150 or more mm. (av. 186 mm.); all 97 patients were over 50 years of age; the decrease in the ratio in cases of high blood pressure is attributed to the cardiovascular changes. In cases of high blood pressure, the impaired excretory function of the kidneys may cause retention of indican. Healthy individuals over 50 years of age, living in the middle states and doing light work, usually excrete from 16 to 20 g. of urea in 24 hrs. In cases of high blood pressure, an excellent daily ration consists of 1 quart of milk, 1 egg, supplemented with a liberal amt. of vegetables, and, at times, a small amt. of meat or fish.

JOSEPH S. HEPBURN

Volhard's water test of function of the kidneys. FRITZ C. ASKENSTEDT. *J. Am. Inst. Homeopathy* 14, 338-9 (1921).—A description of the test, and a discussion of its value in the diagnosis and treatment of arteriosclerosis and renal disease. J. S. H.

The syphilis precipitation reaction of Sachs-Georgi. N. YOSHIMARE. *J. Path. Bact.* 24, 358-60 (1921).—A comparison of discrepancies between the Wassermann and Sachs-Georgi reactions. The latter is frequently negative when the Wassermann is positive.

JOHN T. MYERS

Surface tension and the suppression of shock by sodium hyposulfite. W. KOPACZEWSKI. *Compt. rend.* 173, 451-3(1921).—The new data reported extends to horse serum, the results previously reported (cf. *C. A.* 15, 1572) supporting the idea of a relation between flocculation and surface tension. GEORGE ERIC SIMPSON

Vaccines. ANDRÉ LESURE. *J. pharm. chim.* 24, 93-107, 139-47, 168-83(1921).—A detailed review. S. WALDBOTT.

H—PHARMACOLOGY

ALFRED N. RICHARDS

Chemotherapeutic experiments with acridine preparations on cholera-infected guinea pigs and mice. W. BAUMGARTEN. *Z. Hyg. Infektionskrankh.* 91, 511-37 (1921).—Small doses of diaminocrocinine nitrate and trypaflavine given to guinea pigs infected with cholera show a decided healing action. The therapeutic index, that is the ratio of the smallest active dose to the max. tolerated, was about 1 to 10. A combination of the nitrate with immune serum gives a strong therapeutic action. F. A. C.

Novocaine dermatitis in dentists. C. GUY LANE. Mass. General Hospital. *Dental Cosmos* 63, 878-84(1921).—Novocaine is definitely shown to produce a dermatitis of the hands of individuals who have an idiosyncrasy to this action of the compd.

JOSEPH S. HEPBURN

Sodium methylate as a substitute for sodium-potassium, and sugar lactones as a substitute for strong acids, both in the treatment of root canals. P. A. LEVENE. *Dental Cosmos* 63, 905-6(1921).—A dil. alcoholic soln. of CH_3ONa may be used in the pulp chamber and root canals instead of the alloy of K and Na; it is much less destructive to living tissue, and less liable to produce necrosis of such tissue. The lactones of gulonic and galactonic acids are of value in removing Ca deposits from the pulp canals, since their aq. solns. react with such deposits to form sol. Ca salts. J. S. H.

Technic for use of sodium methylate and lactones in the gaining of access to and the cleansing out of pulp canals. H. E. S. CHAVES. *Dental Cosmos* 63, 906-7(1921).—The use of these compds. is described. Cf. preceding abstr. JOSEPH S. HEPBURN

Diethylrhodanine. C. S. LEONARD. *Medd. K. Vetenskapsakad. Nobelinst.* 4, No. 14, 1-13(1921).—*Synthesis.* $\text{Et}_2\text{CBrCO}_2\text{H}$ was prep'd. by the action of Br and red P on $\text{Et}_2\text{CHCO}_2\text{H}$. Diethylrhodanine was prep'd. by reaction of $\text{Et}_2\text{CBrCO}_2\text{H}$ with NH_3 , dithiocarbamate. The yield ranged from 30% to 54% according to the mode of carrying out the reaction. Diethylrhodanine forms needle-like crystals, m. 107.5° after recrystn., is very sol. in alc., Et_2O , CHCl_3 , and warm fatty oils. At a temp. of 18°, 1 part of the compd. dissolves in 3000 parts of water or in 20 parts of almond oil. It probably forms a Na salt. It tends to decompose on standing in the presence of moisture, liberating objectionable derivs. of S. *Pharmacology.* Expts. were performed on young salmon (*Salmo salar*) and on rabbits. Aq. solns. of the drug were purified by shaking with animal charcoal; a concn. of the drug narcotic to salmon was not obtained within the range of its solv. in water. In all of the expts. on rabbits, the dose of the drug was 0.2 g. per kg. of body wt. Intravenous injection of the drug in an emulsion of gum arabic produced hemolysis and death by respiratory failure. Intravenous injection of a NaHCO_3 soln. of the drug, or intramuscular injection of its soln. in almond oil exerted a narcotic action slightly greater than that of veronal, and produced a similar type of sleep with more rapid recovery. It was apparently without action when administered by mouth. Diethylrhodanine probably will not be of therapeutic value on account of its extremely slight solv. in water, and its inactivity when given by mouth. JOSEPH S. HEPBURN

Comparative effects of morphine and alkaloids of the benzylisoquinoline group on cardiac muscle. P. J. HANZLIK. Western Reserve Univ. *J. Pharmacol.* 17, 445-71 (1921).—Morphine augmented the tone of the perfused amphibian heart, temporarily

increased but later slowed the rate and shortened the amplitude, while papaverine, chelidoneine, hydrastine and narcotine lowered the tone, slowed the rate and reduced or abolished the amplitude of contractions of the perfused hearts. Cotarnine-HCl and hydrastinine possessed action similar to morphine, although individual variations were encountered. Antagonistic effects on cardiac muscle were produced in mixts. and by independent application of the alkaloids. The results indicate the difficulties involved in the correlation of chem. structure and pharmacol. action and the unreliability of classifications derived from limited data. The results of the observations are of value in appraising the importance of the cardiac factor in circulatory collapse resulting from the administration of these drugs or other causes and their therapeutic value in collapse.

C. J. WEST

Pharmacology of chelidoneine, the benzylisoquinoline alkaloid of Chelidonium (celandine or tetterwort) and Stylophorum. P. J. HANZLIK. Western Reserve Univ. *J. Pharmacol.* 18, 63-102(1921).—See *C. A.* 15, 273.

C. J. WEST

I—ZOOLOGY

R. A. GOTTFER

Chemical development of the ovaries of the king salmon during the spawning migration. CHARLES W. GREENE. Univ. Missouri. *J. Biol. Chem.* 48, 59-71(1921).—“Active development of the gonads of the king salmon takes place chiefly after the entrance of the salmon into fresh water. The ovaries increase in wt., during the migration of the spring run on the Columbia River, from 200-300 g. at the beginning to as much as 2,500 g. at the end. From 90-95% of the total wt. of the mature ovaries is acquired while the salmon is not taking food. It is a unique case of synthesis and growth of the tissues of the gonads while all other organs are decreasing by a process analogous to tissue starvation.” The H₂O of the developing ovary is greatest in the mature ovary, 58.3% as compared with an av. of 53.7% in the younger ovaries. The total inorg. salts vary only slightly being 0.57% in the relatively young ovaries and 0.72% in the mature ovaries and ripe ova; the saline content is thus independent of the saline content of the H₂O in which the salmon lives. The av. protein content is 20.7% which is nearly 11% greater than the amt. present in egg yolk; the proteins thus form no inconsiderable part of the stored food of the salmon eggs. The org. extractives are never great in amt., av. 1.53%, of which carbohydrate constitutes 0.09%. The neutral fats represent the chief store of energy in the salmon’s egg, decreasing from an av. of 15% in the youngest ovaries to 10.6% in samples from the spawning grounds. The storage of the proteins and egg oils takes place from the proteins and lipins liberated from supplies in the muscles, liver, connective tissues, etc. The reversible action of the lipases is adequate to account both for the storage of ovarian fats and for their % decrease as the fats are depleted from the body by oxidation during the migration. The mature salmon eggs contain only from 2-3.6% of phospholipins as compared with 11% or more in hen’s egg yolk. Like the neutral fats the phospholipins decrease in amt. with approaching maturity of the ova; the 4% av. for an ovary of 500 g. wt. drops to an av. of 2.6% for mature ovaries weighing 700-2,500 g. The significance of this decrease is not clear. “On the whole it seems evident that the phospholipins play a less dominant role, at least they form a far less proportionate amt. of the stored food materials in the salmon ovaries and eggs than they play in the case of the hen egg. The fats, too, form a smaller % of the food store of the egg. The dependence of the salmon on fats and fatty bodies for energy during the migration is reflected in the partial depletion of both neutral fats and phospholipins in the mature salmon eggs. The proteins are present in unusual amt. and doubtless play a leading part in the nutrition of the developing embryo.” Two samples of mature eggs sepd. from the ovarian

tissue and floating free in the ovarian fluid in the body cavity had the following compn.: H₂O 57.68 and 53.19%; total solids 42.32 and 41.91%; protein 26.56 and 27.01%; phospholipins 1.9 (probably low) and 3.6%; neutral fats 11.7 and 9.15%; total org. extractives 1.43 and 1.41%; inorg. ash 0.68 and 0.62%. A. P. LOTHROP

A chemical study of certain Pacific coast fishes. D. B. DILL. Bur. Chem., Food Research Lab. *J. Biol. Chem.* 48, 73-82(1921).—"Large variations in the compn. of individual fish of several species (yellow fin tuna, blue fin tuna, sahle fish, barracuda, and mackerel) have been found. These variations are frequently erratic and cannot be ascribed to known factors. The mackerel undergoes a seasonal variation in compn.; large mackerel are generally fatter than small mackerel of the same school and the variation in one season may not be paralleled by the next season's variation. The period of max. fat content during 1919 followed the mid-summer spawning season, while the period of minimum fat content preceded the spawning season. In the previous season the % of fat appeared to be at a minimum in the late fall after the spawning season. No evidence of a connection between the sex and the proximate chem. compn. of the mackerel was found. With some exceptions, the mackerel and the mackerel-like fishes were found to have an increasing fat content through the summer and early fall." The max. % of fat found in an individual mackerel was 20.32 and the minimum 0.28. A chemical study of the California sardine (*Sardinia caerulea*). *Ibid* 93-103. "Considerable variation in the compn. of individual sardines of the same size and from the same school may occur. Small sardines were found to have a max. fat content in the summer months. With some exceptions, other factors being the same, the fat content of sardines increases with the increasing size of the fish. Marked variations in the fat content of a seasonal nature were found in large sardines, the % of fat dropping from a max. in December or earlier to a minimum in May. This variation was more extreme in 1918-19 than in the following season. Great differences in the fat content of sardines of the same size from different schools were observed. The migration of schools may be related to the sudden decrease in fat content that takes place in April of each season. No evidence that the growth of the reproductive organs draws to any great extent on the reserve store of fat was obtained. The relation between the % of fat in the sardine and the sea temp., if any, is remote. There are appreciable %s of glycogen in the flesh of the sardine (0.5, 0.17 and 0.22% in 3 detns.)." The av. compn. of an individual large sardine (based on the analysis of 10 individuals in April when the fat content was lowest) was as follows: wt., 165 g.; solids, 21.66; Et₂O ext., 0.89; ash, 1.6; protein, 19.37%. The max. amt. of fat was 21.88% in Dec. and the minimum 0.75% in April.

A. P. LOTHROP

Fertilization and egg-secretions. OTTO GLASER. - Amherst Coll. *Biol. Bull. Marine Biol. Lab.* 41, 63(1921).—The questions discussed are: (1) Do egg-secretions have anything whatever to do with fertilization? (2) How do the exudates act? (3) Is the sepd. lipolysin really a lipolytic enzyme? (4) Is the agglutinin also an enzyme? (5) What is the relation of lipolysin and agglutinin to the specificities of fertilization?

L. W. RIGGS

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Food laws and control during war time. A. BEHRE. *Z. Nahr-Genussm.* 41, 244-61(1921); cf. *C. A.* 15, 3338.—An address reviewing the general subject with a discussion of the regulations affecting each of 17 listed types of foodstuffs. L. D. E.

The preparation of flour from oats. JOHANNES BUCHWALD. *Z. ges. Getreidewesen* 12, 103-6(1921); cf. *C. A.* 15, 1767.—During the war attempts to prep. finished products

from oats without steaming and drying were made in Germany. Prepn. of oat flour is now accomplished by direct milling. The flour is obtained by sifting, giving a yield of 45% through a no. 11 silk gauze with an extra 14-8% through a no. 5 gauze. To obtain the finest flavor, however, the oats must be artificially dried either before or after milling.

C. C. DAVIS

The Humphries process. K. Mons. *Z. ges. Getreidewesen* 12, 89-103(1921).—An attempt to explain for those unfamiliar with colloid chemistry the Humphries-Thomas process for treating and improving the baking qualities of wheat flour. Though the wheat has approx. 1% of H₂O added by this process, the final flour shows an increase of only approx. 0.2% moisture. It is assumed therefore that the H₂O added is adsorbed by the proteins to form a colloidal mass from which the H₂O cannot be removed by physical methods. The H₂O mols. are adsorbed by the proteins and starch by virtue of their surface energy. There are thus 2 opposing forces, that of the surface energy of the flour particles adsorbing the H₂O and that of the H₂O attracting itself and acting in opposition to the first force. Therefore if H₂O is brought in contact with this system (Humphries process) the equil. is displaced in the direction of the adsorptive surface energy of the flour. As a result H₂O is taken up and the flour changes its physical properties. Advantage is taken of the fact that certain acids, acid salts and nitrates accelerate the swelling of the proteins, whereas chlorides, phosphates, sulfates, citrates, tartrates, EOH, sugar, dextrin and certain gums retard this action. By the Humphries process mixts. of 40% wheat poor in gluten and 60% wheat with soft, poor gluten were treated with 0.2-0.3% of (NH₄)₂HPO₄, Na₂HPO₄, Ca₂HPO₄, (NH₄)₂SO₄ or Na₂SO₄. The final baked products were much superior in appearance, finer grained and more elastic than without the salt addition. The increase in vol. was 8-14%. C. C. DAVIS

Frozen eggs. M. MICHAUD. *Bull. soc. hyg.* 9, 415-35(1921).—A discussion of the frozen-egg industry with suggestions for control based chiefly on the publications of the U. S. Dept. of Agr.

H. A. LEPPER

Artificial honey. A. BEYTHIEN. *Z. Nahr.-Genussm.* 41, 300-22(1921); cf. C. A. 14, 1588.—Regulatory recommendations of a committee of food officials and representatives of the industry, chief of which are that artificial honey (Kunsthonig) must be made by the inversion of pure beet sugar with a polarization of not less than + 99, must contain not less than 78% of dry substance and the unchanged sugar content must not exceed 10%. L. D. ELLIOTT

Relation between cold storage and canning of fish. D. B. DILL AND L. H. ALMY. Bur. Chemistry. *Fishing Gazette* 38, 40-1(1921).—When spoiled tuna fish is cooked and canned, the product frequently has a characteristic honey-comb appearance, a bad flavor, and a peculiar biting odor. When tuna is frozen slowly in air (at a temp. slightly below 32° F. or even as low as -8° F.), and is subsequently canned, the product has a characteristic pitted appearance, more or less similar to the honey-comb appearance just mentioned; but its flavor does not differ from that of a product prepd. from fresh unfrozen tuna. The pitting apparently becomes more pronounced as the period of storage of hard-frozen tuna prior to canning is increased. JOSEPH S. HEPBURN

Utilization of fishery by-products. D. B. DILL. Bur. Chemistry. *Fishing Gazette* 38, 45-6(1921).—A discussion of the manuf. of fish meal and fish oil as by-products of the canning industry with special reference to the canneries of southern California. A fish meal for use as poultry or hog feed should have a low content of both moisture and fat, be made from fresh material fit for animal food, and be free from a scorched odor. Analyses of 7 samples of tuna-fish meal showed a range of moisture from 2.58% to 8.00%, of oil from 7.09% to 25.89%, of P₂O₅ from 5.64% to 13.85%, and of N from 7.61% to 9.12%. A large proportion of the N is lost during the pressing in the manuf. of the meal; the loss is greater with a screw press than with a hydraulic

press; a sample of liquor from a screw press contained 2.22% N. For the production of a high-grade fish oil, fresh material must be used, the press liquor must be as free as possible from suspended matter, and the conveyors and separating tanks must be cleansed and sterilized daily. Fish oil darkens rapidly and becomes hydrolyzed when fish becomes stale. This decompos. is less rapid in cooked fish or in expressed oil stored in a clean container at a low temp. The color, odor, and acidity of the oil are not materially influenced by prolonged pressure cooking. With care, a pale yellow oil may be obtained containing less than 1% of free acid calcd. as oleic; at the other extreme are dark brown oils of foul odor and containing from 10% to 25% of free acid.

JOSEPH S. HEPBURN

Analysis of food fishes. L. H. ALMY AND ELMER FIGLO. Bur. Chemistry. *Fishing Gazette* 38, 42-3 (1921).—The following data are given for 11 species of fish caught in the Gulf of Mexico and analyzed immediately: Edible portion as % of total wt., compn. of flesh (including % of moisture, protein, fat, and ash), food value in cal. per lb. of whole fish and of edible portion. The edible portion ranged from 39% to 66% of the total wt. The protein ranged from 18.63 % to 21.50% of the flesh, the fat from 0.18% to 14.92%, the moisture from 65.12% to 80.08%, the ash from 1.19% to 1.51%; a high fat content was usually accompanied by a low moisture content and vice versa. The fat of 2 species was analyzed with the following results: *Spanish mackerel*. Sp. gr. 0.9187, I number 131.0, saponification number 199.2, acid value 7.5. *Roe mullet*. Sp. gr. 0.9184, I number 107.7, saponification number 199.2, acid value 5.1.

JOSEPH S. HEPBURN

Chemistry of milk curd modification. R. W. TERRY. *Arch. Pediatrics* 38, 465-90 (1921).—The following conclusions are reached. Cow milk is modified on account of the great difference in the physical condition of the curd yielded by it and of that yielded by human milk. The casein of human milk and that of cow milk probably are identical. Coagulation is due to "the combined action of rennin and Ca ions, each acting independent of the other." Freshly formed curds possess, but rapidly lose, a powerful cohesive property. Diln. of milk with water modifies the curd by producing a decrease in the concn. of the active masses. Gruels and cereal decoctions function as protective colloids by virtue of the gelatinized starch which they contain. Lactose apparently favorably modifies the curd; other sugars have little influence on its character. Boiling of milk removes Ca salts as a scum forms; and the character of the curd is thereby profoundly altered. Citrates fix Ca ions and thereby influence the formation of the curd. Alkalies ppt. Ca salts, and thus reduce the concn. of one of the active masses. KOH or NaOH, in dil. soln. of known concn., e. g., 1%, are desirable modifying agents. Lime water causes pptn. of Ca, and gives rise to a curd with very desirable properties. Milk of magnesia influences curd formation in the same way as lime water, but acts more slowly. "No single method of modification produces the ideal curd. This can only be accomplished by a combination of diln. to the proper caseinogen concn., the addition of a citrate to establish the correct Ca : citrate ratio, the adjustment of the mineral constituents, the addition of an alkali to reduce the acidity and properly stimulate gastric secretion, and by the addition of a protective colloid to establish the correct casein: lactalbumin ratio." A bibliography is appended. J. S. H.

The variation in the percent of fat in successive portions of cow milk. A. C. RAGSDALE, SAMUEL BROOK AND CHAS. W. TURNER. *J. Dairy Sci.* 4, 448-50 (1921).—Data are given to show that the longer a cow stands quietly before milking the greater the variation in fat in successive portions of the milk. The same is true of milk standing in a cylinder.

H. A. LEPPER

Manufacture of cow milk Roquefort cheese. K. J. MATHISON. U. S. Dept. Agr., Bull. 970, 1-28 (1921).—This bulletin deals with the properties and compn. of French

Roquefort cheese which is a product of sheep milk, and with the modifications in the process which have been found to give best results in the manuf. of domestic Roquefort cheese from cow milk.

W. H. Ross

Goat milk. JOSEPH K. CALVIN. *Arch. Pediatrics* 38, 584-91(1921).—A discussion of the chem. compn. of goat milk, and of its use as a food, especially in the artificial feeding of infants. A bibliography of 38 references is appended. JOSEPH S. HEPBURN

Method for determining lime in dairy products. T. MOJONNIER. *J. Dairy Sci.* 4, 453-5(1921).—Bring the sample, weighed or measured into a Babcock bottle, to 18 g. with H₂O. Mix, add 15 g. H₂SO₄, centrifuge 10 min., float off all fat with H₂O. Transfer the soln. to a beaker, wash the bottle 3 times (H₂O), add 2 vol. alc., let stand overnight, filter on a Gooch crucible with asbestos, wash with alc., dry, ignite to const. weight, weigh as CaSO₄. The residue from a Mojonnier fat-extn. flask can be neutralized with H₂SO₄, 2 vols. alc. added and the detn. completed as above. The method is simple and accurate but cannot be used in the presence of a large amt. of sucrose.

H. A. LEPPUR

The utilization of the Argentine thistle (REWALD) 27. The hermetisator (SCUNDEK) 1. A chemical study of certain Pacific coast fishes (DILL) III.

Drying fruits and vegetables. B. S. HARRISON. U. S. 1,387,710, Aug. 16. Fruits or vegetables, e. g., potatoes, are sliced, treated with a soln. of NaCl to prevent oxidation and then dried in CO₂ or N or other inert or non-oxidizing gas, to preserve them so that H₂O will restore them to a condition similar to the fresh raw material.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The relation of chemical training to industry. WALTER H. COOLIDGE. *Science* 54, 367-71(1921).

E. H.

The future of British chemical industry. WILLIAM J. POPP. *Chem. Age* (N. Y.) 29, 399-401(1921).

E. H.

Large-scale chemistry at the Imperial College of Science and Technology. J. F. T. NATURE 107, 824-7(1921).—An illustrated description of the equipment for teaching used in this institution.

W. H. Ross

Chemical industry power and fuel data. H. GOODWIN, JR. *Chem. Met. Eng.* 25, 708-9(1921).—The Bureau of the Census has cooperated with the U. S. Geol. Survey in the prepn. of a Report of a Superpower System for the Boston to Washington Region, which will be issued shortly. The present article contains an analysis, in the form of two tables, of the fuel and power used by the chem. and allied industries situated within the superpower zone. The figures will serve to supplement those given in *Ibid* 25, 470(1921).

E. G. R. ARDAGH

Handling liquid chlorine. D. K. BARTLETT. *Chem. Age* (N. Y.) 29, 397-8(1921).

E. H.

Evaporation by vapor compression. BURTON DUNGLINSON. *Chem. Met. Eng.* 25, 246-7(1921).—In multiple-effect vacuum evaporator practice, the av. temp. difference, vapor to liquid, is 25°. If this thermal head is secured by vapor compression, a minimum pressure increment of 20 lbs. per sq. in. must obtain. To lower this thermal head and increase heat transmission, high velocity film evapn. is used in the *Soderlund Boberg* design which is described (2 cuts). One multistage turbo compressor serves 3 effects. In evapg. sea water the ratio of evapn. is 12 lbs. H₂O to 1 lb. steam (cf. C. A. 15, 2021).

C. C. HERITAGE

Economy of modern grinding methods. HARLOWE HARDINGE. *Chem. Met. Eng.* 25, 229-32(1921).—Grinding problems are classified as wet or dry. These are subdivided into granular (4-mesh), medium fine (20-mesh), fine (200-mesh) and extremely fine. Choice of grinding equipment should depend on ultimate operating cost per ton ground. Detailed estimates of operating costs of modern *versus* old types are given, the totals being \$0.18 and \$0.55 per ton, resp. Delays are considered on the basis of profit lost thereby.

C. C. HERITAGE

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

American standards for quality of water. J. J. HINMAN, JR. *J. Soc. Chem. Ind.* 40, 325-7R(1921); cf. *C. A.* 14, 2830.—The standards of the International Joint Commission and the U. S. Treasury Dept. which are in general use in Canada and America are carefully outlined, together with tables showing the attitude of State water labs. and officials of individual water plants toward quality standards. Evidences show a close agreement of the interpretation of bacterial analyses in America and France and point to a closer agreement between American and English standards than indicated in the review which occasioned the writing of this article.

G. C. BAKER

Boiler feed water purification. WM. M. TAYLOR. *Chem. Met. Eng.* 25, 640-1 (1921).—This is a criticism of Appelbaum's article (*C. A.* 15, 3355). T. maintains that zeolitic softeners do not furnish waters of zero hardness; they contain as much as 0.50 grains per gal. of hardness when expressed in terms of CaCO_3 . There is an increased tendency for foaming, owing to the increased Na salts, especially Na_2CO_3 , which under the influence of steam pressure may break up and form volatile org. acids that exert a corrosive action. The advantages of zeolitic softeners are overestimated, and the disadvantages of boiler compds. given greater wt. than they possess. Cf. *C. A.* 15, 911.

G. C. BAKER

Some practical applications of the theory of biological purification of waste liquors. GUY P. TATHAM. *J. Soc. Chem. Ind.* 40, 201-2T(1921).—The measure of pollution in a waste liquor is dependent upon the O required for its complete oxidation, and the rate of absorption of the dissolved O is proportional to the concn. of the polluting material. A numerical measure of the activity of the biol. oxidation may be designated by α ("avidity constant") which is dependent on the kind of liquor being dealt with, and the circumstances under which the oxidation is taking place. Mathematical deductions are made showing the percentage purification attained during a mean time of contact. The equation involves these two variables and the avidity const. If the avidity const. is detd. for any waste liquor, and the degree of purification desired is known, the necessary mean time of contact may be calcd., and the plant designed to give the indicated time of contact. Exptl. evidence in support of the calcns. is given.

G. C. BAKER

The sewage-testing station of the Ill. State Water Survey Division. EDWARD BARTOW. *J. Ind. Eng. Chem.* 13, 945-6(1921); cf. *C. A.* 15, 2142.—Brief descriptions are given of the screening, pumping, aeration, sludge sepn., effluent disposal, sludge dewatering, and sludge-drying units. The Dorr-Peck modification of the activated-sludge process will first be studied; other methods of sewage disposal will be studied later.

G. C. BAKER

The utilization of sewage sludge. JOHN D. WATSON. *J. Roy. Soc. Inst.* 42, No. 2, Sept., 90-6(1921); *Public Health Eng. Absts.* Oct. 8(1921).—Economic features of grease extn. from sludge are discussed. Analyses show that farmyard manure is superior to ordinary sewage sludge as a fertilizer. To make sewage sludge available for fertilizer purposes further investigation is suggested (1) to obtain it from sedimenta-

tion tanks before putrefaction, (2) to eliminate as much grease as possible, (3) to eliminate as much moisture as possible, (4) to appraise it at its true value. W. believes that the growing knowledge of colloids will make available the high N content of activated sludge for fertilizer purposes, analyses showing that activated sludge is superior to farm manure as a fertilizer. The process of blowing O₂ at atm. air, through septic sewage, which is in active state of fermentation, and utilizing the gas liberated to form an explosive gas are being successfully tried by several power gas plants in Australia. Birmingham, England sewage sludge obtained by a biologic process and subsequently air-dried was successfully employed to augment coal slack used in Lancashire boilers. Birmingham tests showed one lb. of air-dried sludge will evap. at least one lb. of water. There is, however, considerable ash and a tendency for the sludge to flux and adhere to the furnace bars. Such use of sewage sludge is considered remunerative where there are means of utilizing it in the immediate vicinity of the drying locality for steam raising and electric power generation. Discussion of advantages and disadvantages of applying wet sludge through pipe lines directly onto the fields are given. G. C. B.

Power gas from sewage. J. D. WATSON. *Engineering* 112, 456(1921).—Tests upon Birmingham sewage show that it is practicable and economical to utilize gas emanating from sewage to drive an ordinary suction gas engine. The chief gaseous constituents from septic sewage are CH₄, H₂, N₂, and CO₂, but the CH₄ is the important factor. W. believes the gas comes largely from the sewage sludge and not the liquid sewage. There was an entire absence of odor. G. C. BAKER

Oil-camp sanitation. C. P. BOWIE. Bur. Mines, *Tech. Paper* 261, 32 pp.(1921).—By proper organization sanitary conditions may be maintained in newly opened oil fields. G. C. BAKER

Handling liquid chlorine (BARTLETT) 13. The destruction of cement and of concrete conduits and masonry for sewage canals (SPLITTERGERBER) 20.

Softening water. J. B. WHERRY. U. S. 1,388,133, Aug. 16. A H₂O-softening material is prepd. by heating a natural clay having base-exchanging properties to a temp. (usually about 700°) sufficiently high completely to dehydrate the material without fusion and then rehydrating the material with an aq. soln. contg. NaOH. The clay may be preliminarily purified with NaCl soln. and NaOII soln.

Treating water with chemical reagents. J. S. SIMSOHN. U. S. 1,388,813, Aug. 23. The addition of Na₂CO₃ or other treating agents to water flowing through a conduit is automatically regulated by elec. devices, depending on the rate of flow and cond. of the H₂O.

Removing gases from water. J. J. WILSON. U. S. 1,387,748, Aug. 16. Gases are discharged from H₂O by feeding it into a closed vented tank through a coil in the tank discharging at the liquid level. H₂O is drawn off from the bottom of the tank.

Apparatus for distilling sea water on shipboard. W. L. DE BAUFRE. U. S. 1,387,475-6, Aug. 16.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER AND ALBERT R. MERZ

Bechhold's "capillary phenomenon" in agriculture. JEROME ALEXANDER. *Science* 54, 74(1921).—The observation of Bechhold (*C. A.* 15, 458) that when a porous mass is soaked in the soln. of a salt and then dried the salt collects almost quantitatively at or near the exterior surfaces, which Kraus (*C. A.* 15, 2222) has shown to be dependent upon evapn. at the exposed surfaces, is suggested as the scientific reason for the value of cultivation in agriculture. H. J. C.

Science and crop production. E. J. RUSSELL. *Nature* 108, 116-20(1921).—A discourse. W. H. ROSS

Phosphorus in fertilizer. WILLIAM H. WAGGAMAN. U. S. Dept. Agr., *Year Book* (Separate) 840, 217-24(1920).—A plea for more conservative and scientific methods in the production of sol. phosphates from phosphate rock. W. H. ROSS

Getting our potash. WILLIAM H. ROSS. U. S. Dept. Agr., *Year Book* (Separate) 851, 363-76(1920).—A review of progress made in the production of K₂O in the United States. Of the total of 17,700 tons produced during the period, 1915-1920, 10% was obtained from insol. K₂O deposits, 70% from sol. deposits, and 20% from org. materials. W. H. ROSS

The phosphate industry. II. Superphosphates. W. PACKARD. *J. Soc. Chem. Ind.* 40, 304-6R(1921); cf. *C. A.* 15, 3807.—A brief review of the principles underlying the phosphate industry. R. B. DERMER

Treating plants with waste gases containing carbon dioxide. FRIEDR. RIEDEL. *Chem. Ztg.* 45, 829-30(1921).—Further replies to Claassen's objections. Cf. *C. A.* 15, 2328. T. G. PHILLIPS

Phosphate rock (WAGGAMAN) 18. The utilization of sewage sludge (WATSON) 14. Alsatian salts of potash (BEAUVERRIE) 18.

16—THE FERMENTATION INDUSTRIES

H. S. PAYNE

Industrial alcohol. JAMES M. DORAN. *Paint, Oil and Chem. Rev.* 70, No. 19, 7-8(1920); *Chem. Age London* 4, 72(1921).—An historical outline of the development of the alc. industry in the U. S. and its relation to the National Prohibition Act. C. C. DAVIS

Contribution to the history of beer. ERNST A. KUHN. Munich. *Z. tech. Biol.* 8, 194-216(1921).—The story of the brewing of beer from its earliest use to the 19th century. Many references are given to the early literature on this subject. F. A. C.

The concentration and purification of alcoholic fermentation liquors. I. The distillation in steam of certain alcohols. JOS. REILLY AND WILFRED J. HICKINBOTTOM. *Sci. Proc. Roy. Dublin Soc.* 16, 233-47(1921).—The work of other investigators on the distn. of aq. solns. of the lower aliphatic alcohols is discussed. The authors distd. dil. aq. solns. of MeOH, EtOH, PrOH, BuOH, iso-BuOH, sec-BuOH and iso-AmOH in an app. arranged to keep the vol. of liquid in the distn. flask const. by adding water at the same rate as the liquid distd. out. Usually 200 cc. of soln. was used and the distillate was collected in fractions of 5 or 10 g. Each fraction was analyzed either by detn. of sp. gr. or by detn. of the amt. of standard K₂Cr₂O₇ + H₂SO₄ soln. necessary to oxidize the alcohol. The value of the distn. coeff. *K* was calcd. for each fraction. If *a* = the initial amt. of alc. in the flask, *x* = amt. of alc. in distillate after vol. *v* has distd., and *V* = const. vol. of liquid in the flask; *K* = *A* × *V* × 2.3026 where *A* = $(1/v) \log [a/(a-x)]$. The values of *K* found for EtOH agreed with those found by Sorel (*Compt. rend.* 116, 693(1892)) who distd. without keeping the vol. const. The value of *K* for each alc. varies with the concn. The higher alcs. distil from dil. aq. solns. more rapidly than do MeOH and EtOH. The distn. coeff. increases in an approx. regular manner with increase in mol. wt. The occurrence of a branched chain in the compd. results in increased volatility. A comparison of the values of *K* with the vapor pressures at 100° of the various alcs. shows that there is no apparent agreement between the rates of distn. and the volatility of the alcs. In the estn. of BuOH by the oxidation method the odor of an ester was sometimes detected. This reaction was studied as a sep.

problem. By slowly adding BuOH 148 g., to $K_2Cr_2O_7$ 200 g. dissolved in a mixt. of H_2SO_4 276 g., and water 750 g., and heating on the water-bath for 2–6 hrs. after the violent first reaction had quieted down, butyl butyrate was formed in 75% of the theoretical amt. Some free BuOH and butyric acid were present and a small amt. of unidentified substance with a high b. p. The ester also contained in soln. a green Cr compd., which remained after distn. of the ester as a dark green amorphous mass sol. in acetone.

L. E. GILSON

The influence of electric potential upon the velocity of fermentation. M. C. POTTER. *Proc. Univ. Durham Phil. Soc.* 6, 16–21(1915–1920).—Carefully controlled expts. showed the elec. potential to have no influence upon the velocity of yeast fermentation.

BURTON G. PHILBRICK

The government acetone factory, Nasik Road. A. APPLEYARD. *J. Indian Ind.* 1, 267–81(1921).—An illustrated description of the plant and process for production of acetone by fermentation.

E. H.

Seed-culture methods in the production of acetone and butyl alcohol by a fermentation process. HORACE B. SPEAKMAN. *Toronto Univ. J. Ind. Eng. Chem.* 12, 581–7(1920).—The prepn., fermentation and distn. of the raw material has been already described (*C. A.* 13, 2197). The max. yield in the minimum hrs. depended upon the (1) correct ratio between the vols. of seed-culture and mash; (2) stage at which a culture should be withdrawn for new seed and (3) no. of generations between the subculture and the fermentation for max. efficiency. A seed tank unit of 500 gal. was used to inoculate a fermenter of 24,000 gal. During fermentation the acidity first rises, then falls. The culture in the seed process was transferred to the next fermentation batch when the acidity started to fall. The no. of generations between spore culture and fermentation was reduced to a minimum and the time of fermentation thereby reduced from 48 to 30 hrs. The culture plant and its operation are described and illustrated in detailed fashion.

C. C. DAVIS

Formation of glycerol from sugar. W. TAEGENER. *Centr. Zuckerind.* 28, 289–9 (1920).—An historical review of the theory of fermentation leading up to Wohl's theory of the formation of glycerol through glyceraldehyde and dihydroxyacetone. The process of Connstein and Lüdecke of fermenting sugar in a medium made alk. with Na_2SO_3 is briefly described.

NICHOLAS V. S. MUMFORD

A method of treatment of white wines. L. MONNIER. *Ann. chim. anal. chim. appl.* 2, 147–8(1920).—Analysis of white wines leaving a blue powdery residue proved the latter to be Prussian blue. $K_3Fe(CN)_6$ and gelatin were evidently used as clarifiers, a modification of the German method of using a Zn salt salt and $K_3Fe(CN)_6$. C. C. D.

Identification of tartaric acid in wines. L. MATHIER. *Ann. chim. anal. chim. appl.* 3, 270–1(1921); cf. *C. A.* 14, 3748.—Previous methods are fallacious because they assume that if free tartaric acid (A) is present that all K exists as $KHC_4H_4O_6$ (B). AmOH (C) was found to remove A from wine without dissolving B or $CaC_4H_4O_6$. Procedure: 20 cc. of wine are shaken with 20 cc. of C to form an emulsion, it is allowed to stand, and the C soln. pipetted off. The latter is shaken with an equal vol. of H_2O , the H_2O soln. removed and evapd. to dryness. It is then dissolved in 5–6 cc. of H_2O and a drop of $CaCl_2$ (150 g. per 1. of $CaCl_2 \cdot H_2O$ + 40 g. of NH_4Cl) and 2 cc. of $L(NH_4)_2C_4H_4O_6$ (2 g. per 1.) are added. A ppt. signifies A. 0.5 g. of A per 1. of wine can be identified thus.

C. C. DAVIS

The multiplying power of yeast at different degrees of acidity. OLOF SVANBERG. Stockholm. *Z. techn. Biol.* 8, 1–22(1920).—An extended study of the acid production of 5 different yeasts growing in beer wort and a detn. of the optimum conditions for rapid growth of yeast. The gas-chain method of Michaelis was used to det. the pH . The acid production is greater than can be explained by the CO_2 formed. There seems

to be no relation between acid production and acid tolerance. The optimum conditions for the development in wort are given as follows: *top yeast S. B.* p_H 3-6. *Bottom yeast H.* p_H 4-6. The same conditions hold for *S. validus* and *S. thermophilorum*. For *Torula* p_H 2.5 and p_H 6 is optimum. The same p_H conditions for yeasts growing in beer wort are optimum when grown in solns. of NH_4 salts and phosphates. F. A. C.

Apparatus for dealcoholizing beer. W. J. RUFF. U. S. 1,387,870, Aug. 16. Beer to be dealcoholized is heated and treated with warm air while circulated in the form of films and cascades over and between a series of superposed plates in a distg. column connected with a condenser and vacuum pump.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Active principles of some plants employed in popular medicine: their investigation by the biochemical method. E. BOURGUEROT. *Bull. soc. chim. biol.* 3, 71-84(1921).—A review. A. T. CAMERON

The culture of ipecacuanha root. P. VAN DER WIELEN. *Pharm. Weekblad*, 58, 1334-55(1921).—A review. A. W. DOX

Arsphenamine. M. TOUSSAINT. *Chimie & industrie* 6, 296-304(1921).—A detailed description of the method of prep. arsphenamine from aniline, with an outline of its chem. properties, tests, methods of analysis, and method of use, and also of the prepn. of *nearsphenamine*. Numerous references are given. A. PARDEAU-COUTURE

Modified method for the determination of bismuth in magma bismuth. U. S. P. IX. M. CRANE AND E. C. MERRILL. *J. Am. Pharm. Assoc.* 10, 606-7(1921).—In place of the U. S. P. IX method C. and M. prep. a Gooch crucible in the usual way and place it in a porcelain crucible provided with a cover. Both are dried and weighed. About 20 g. of the magma are poured into the crucible, the cover of the outer crucible is replaced and the whole weighed. The crucible is placed in a suction funnel and the H_2O sucked out. The crucible is then heated slowly to remove H_2O and the residue dried and heated to redness. The outer crucible is dried and the completed app. weighed. The method reduces the time of assay to about 33% of that of the U. S. P. method.

L. E. WARREN

Notes on the ash yield of glycyrrhiza. C. H. ROGERS AND E. L. NEWCOMB. *J. Am. Pharm. Assoc.* 10, 607-9(1921).—The total ash and the acid-insol. ash of 25 samples are tabulated. The total ash varied from 2.63 to 7.17% and the acid-insol. ash from 0.15 to 3.26%. The max. values were obtained from a specimen of siftings which gave, resp., 34.30 and 19.33%. Also a specimen of commercial drug gave 12.14 and 4.21%, resp. This specimen proved to be mostly senna. From the tabulation it appears that any specimen yielding over 5% of ash or over 3% of acid-insol. ash should be regarded with suspicion.

L. E. WARREN

Determination of nitrates in bismuth salts (McLACHLAN) 7. Viscous petroleum oil mixture (U. S. pat. 1,388,832) 22. Decolorizing viscous hydrocarbon oils (U. S. pat. 1,388,835) 22. Purifying hydrocarbon oils (U. S. pat. 1,387,835) 22.

Preserving digitalis. F. W. HENY. U. S. 1,388,429, Aug. 23. Comminuted desiccated digitalis leaves are compressed into porous tablets and the tablets are packed in a receptacle contg. a desiccating agent such as lime sepd. from the tablets by a layer of cotton.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Elements of the superconcentration of nitric acid. ERNST GALLE. *Chem. Met. Eng.* 25, 741-6(1921).—See *C. A.* 15, 2339.

E. H.

The manufacture of nitric acid by the pot process. H. W. WEBB. *J. Soc. Chem. Ind.* 40, 212-20T(1921).—Several series of distns. were made (1) in glass with pure materials, (2) in a small cast iron retort with commercial materials and (3) on full manufg. scale, to study the effect of acid strength, the charging ratio (wt. H_2SO_4 : wt. $NaNO_3$) and the heat treatment on the strength and yield of nitric acid obtained. Even in (1) the first reaction, beginning at approx. 80° and becoming vigorous at 85°, was characterized by the evolution of nitrous fumes: this phenomenon is hence not due to impurities. A second vigorous reaction begins at approx. 120° and is complete at approx. 150°. In (1) and (2) the residue must be heated to 200° to lower its N content to a point comparable with usual works practice. In (2) it was found that considerable Fe was dissolved from the retort, the Fe in the niter cake being 1.55%, when the niter contained 0.07% and the recovered sulfuric acid used in decomposing it 0.15%. In both (1) and (2) N_2O was produced toward the end of the distn., but in (1) the $N_2:O_2$ ratio decreased during the distn., whereas in (2) it increased. In (2), also, NO was formed in increasing quantity toward the end of the distn. Actual gas analyses are given. The following conclusions are drawn: From the yield standpoint the best strength of sulfuric acid to use is 90-92% and the total yield increases as the charging ratio is increased (1, 2 and 3). The amt. of nitrous acid in the distillate increases as the strength of the H_2SO_4 increases (1 and 2). The amt. of N retained in the niter cake increases with the concn. of the H_2SO_4 , but is unaffected by the charging ratio (1 and 2). The concn. of the distillate is greater, the stronger the charging acid (1 and 2), but the charging ratio has no effect on the strength of distillate (2 and 3). The "blow" becomes less marked as the strength of the charging acid decreases (2 and 3). Neither the total yield nor the strength of the distillate is affected by the rate of distn. (1 and 2). W., therefore, concludes that it is false economy to aim at niter cake acidities of 28-30%, but that 35% is preferable. A number of tables and graphs are included, which must be consulted for details.

F. C. Z.

The influence of gaseous impurities on the catalytic oxidation of ammonia gas. EUGÈNE DECARRIÈRE. *Compt. rend.* 172, 1663-6(1921); cf. *C. A.* 14, 2395.—When H_2S is added to the mixt. of NH_3 and air, it decomposes partly to S and H_2 before reaching the Pt catalyst; expts. were, therefore, made first with H alone. Small quantities of H (0.44% of the gas vol.) increase the activity of the catalyst, whereas more H (1-1.5%) decreases the yield on account of the smaller proportion of O_2 in the gas-mixt. The poisonous action of the H_2S depends less on the total amt. of H_2S passing the catalyst, than on its proportion in the gas mixt.; small quantities of H_2S (0.11%) have only little influence, whereas 2% H_2S decreases the yield 20%. If the catalyst has been poisoned by a gas rich in H_2S , its activity is only very slowly recuperated by an air- NH_3 mixt., but if little H is added to the mixt. the catalyst regains quickly its original activity. These expts. prove that the poisoning of the catalyst in the technical oxidation of NH_3 from cyanamide cannot be caused by H_2S , because this gas mixt. contains only 0.002% H_2S .

E. FIERTZ

The influence of gaseous impurities on the catalytic oxidation of ammonia gas. EUGÈNE DECARRIÈRE. *Compt. rend.* 173, 148-51(1921).—(See above abstract.) C_2H_2 is much more poisonous to a Pt catalyst than H_2S , because the degree of poisoning depends on the total quantity of C_2H_2 passing over the catalyst; the poisoned Pt does not regain its former activity if the pure NH_3 -air-mixture is passed over it.

But if a small quantity of H_2S is added to the gas-mixture besides the C_2H_2 (0.02% H_2S , 0.18% C_2H_2), the catalyst is only very little poisoned, as if only the H_2S were present. Because these two gases occur together in that proportion in the technical NH_3 from cyanamide, the C_2H_2 cannot be the cause of the poisoning of the catalyst. E. FIGGZ

Alsatian salts of potash. J. BEAUVIGIE. *Rev. gen. sci.* 30, 411-2(1919). Bourcier. *Bull. Assoc. Italofrançaise expansion économique* 2, No. 11, 29-30(1919); *Bull. Agr. Intelligence* 10, 832-4.—A review of the early development, geology and compn. of the Alsatian K_2O deposits with statistics on the world's consumption of K_2O . W. H. Ross

Potash. FREDERICK W. BROWN. *Mineral Ind.* 29, 565-75(1920).—Sources and production of potash are treated, and a bibliography is given. A. BUTTS

Potash in 1920. M. R. NOURSE. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 97-12T (preprint No. 18, published Oct. 4, 1921). E. H.

Methods for the complete utilization of niter cake. W. H. H. NORRIS. *J. Soc. Chem. Ind.* 40, 208-12T(1921); cf. *C. A.* 15, 3384.—A brief review is given of various proposals for utilizing niter cake, together with a fairly extensive bibliography. A new process is then described, which depends on solubilities in the system Na_2SO_4 , $(NH_4)_2SO_4$, H_2SO_4 , H_2O , whereby alternately anhydrous Na_2SO_4 is pptd., and then $(NH_4)_2SO_4$. Practically, a mother liquor contg. 5800 lh. H_2O , 5800 lh. $(NH_4)_2SO_4$, 2295 lh. Na_2SO_4 and 318 lh. acidity as H_2SO_4 is heated to 90° and 5500 lh. granular niter cake is added. Its full content of 3880 lh. Na_2SO_4 is thereby sepd. anhydrous, 1670 lh. H_2SO_4 going into soln. This acid soln. is then used to absorb NH_3 , being first dild. by the addition of 6700 lh. H_2O . Having absorbed 577 lh. NH_3 , 9300 lh. H_2O is evapd. in a vacuum evaporator, and 2240 lb. $(NH_4)_2SO_4$ is crystd. out by cooling. The mother liquor and washings are returned to digest a fresh charge of 5500 lh. niter cake. The sodium sulfate analyzes 95% Na_2SO_4 , 0.04-0.15% H_2SO_4 and 0.24-0.39% $(NH_4)_2SO_4$, with less than 0.05% Fe. The ammonium sulfate is also of good color and analyzes 24.47% NH_3 (95% $(NH_4)_2SO_4$), 2.5% Na_2SO_4 , 0.29% H_2SO_4 and 1.5% H_2O . A plant was operated 4 months in England; the wear and tear was light, the action of the acid liquor on iron being less than that of 30% acid; on lead it has no action. Costs are given for a plant to work up 5 tons niter cake per day in England, which shows the process to be even more favorable under normal conditions than in war. *Niter cake granulation* was effected in graining kettles, at a cost of 8 s. 2 d. per ton, including amortization and interest. F. C. Z.

The industrial fixation of nitrogen; a few observations on the Haber process. GEORGE W. TODD. *Proc. Univ. Durham Phil. Soc.* 6, Pt. I, 1-7(1920).—This paper discusses (1) the advantages that would arise from the use of low-temp. catalysts in the fixation of N by the Haber process, and (2) the condensation process of removing the NH_3 from the mixed gases. Curves are given which show the percentages of NH_3 that would be condensed at different temps. and pressures. W. H. Ross

Sodium salts. CHESTER H. JONES. *Mineral Ind.* 29, 623-36(1920).—A statistical review of the industry. A. BUTTS

Borax. A. T. WARD. *Mineral Ind.* 29, 67-9(1920).—World's production and sources and output in the U. S. are outlined, with notes on uses of B compds. A. B.

Phosphate rock. WM. H. WAGGAMAN. *Mineral Ind.* 29, 531-45(1920).—A review of the world's resources and production, with notes on technical development and a bibliography. A. BUTTS

Fluorspar. HUBERT W. DAVIS AND RAYMOND B. LADOO. *Mineral Ind.* 29, 228-37(1920).—Mining, production, and trade conditions are discussed. A. BUTTS

Cryolite. ANON. *Mineral Ind.* 29, 225(1920).—Statistics of production and U. S. imports. A. BUTTS

Magnesite. SAMUEL H. DOLBEAR. *Mineral Ind.* 29, 437-42(1920).—Statistical review of magnesite and Mg. A. BUTTS

Bauxite. T. POOLE MAYNARD. *Mineral Ind.* 29, 19-23(1920).—Production in the U. S. and other countries is outlined, with notes on the use and data on Al salts. A. B.

Monazite. SYDNEY J. JOHNSTONE. *Mineral Ind.* 29, 469-77(1920).—The sources and world's production of monazite and Th products are treated, with notes on technology and bibliography. A. BUTTS

Arsenic. A. E. WELLS. *Mineral Ind.* 29, 35-41(1920).—A review of the industry in the U. S. and foreign countries, with discussion of the metallurgy and uses of As and its compds. A. BUTTS

Selenium and tellurium. *Mineral Ind.* 29, 621-2(1920).—A review of the industry. A. BUTTS

Bromine and iodine. A. T. WARD. *Mineral Ind.* 29, 70-1(1920).—Outline of sources, uses, and amnts. produced. A. BUTTS

Barium and strontium. J. B. PIERCE, JR. *Mineral Ind.* 29, 53-63(1920).—Production and trade in barytes, Ba chemicals, and Sr ores are reviewed, with tables of costs, sales, imports, etc. A. BUTTS

Sulfur, pyrite and sulfuric acid. A. E. WELLS. *Mineral Ind.* 29, 636-51(1920).—A statistical review, with notes on technology. A. BUTTS

The gulf coast sulfur industry. ALBERT G. WOLF. *Eng. Mining J.* 112, 606-8 (1921). E. H.

The strength of hydrogen peroxide solutions. D. VAN OS. *Pharm. Weekblad* 58, 1285-7(1921).—To avoid confusion, the strength of H_2O_2 solns. should be expressed as percentage by wt., since percentage by vol. refers to vol. of available O. A. W. DOX

Carbon black produced from natural gas in 1920. E. G. SIEVERS. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 145-9(preprint No. 16, published Oct. 13, 1921). E. H.

Graphite. B. L. MILLER. *Mineral Ind.* 29, 326-49(1920).—Trade conditions and output in the U. S. and foreign countries are discussed, with review of publications. A. BUTTS

Mica. J. VOLNEY LEWIS. *Mineral Ind.* 29, 450-7(1920).—A review of the world's deposits, production, and trade. A. BUTTS

Fuller's earth. ANON. *Mineral Ind.* 29, 287-40(1920).—Output, trade, and deposits in the U. S. and foreign countries are treated. A. BUTTS

Talc and soapstone. FREDERICK B. PECK. *Mineral Ind.* 29, 652-8(1920).—Production, imports, and talc in foreign countries are discussed. A. BUTTS

Asbestos. OLIVER BOWLES. *Mineral Ind.* 29, 42-9(1920).—A discussion of progress in the asbestos industry, giving statistics of production and trade. A. BUTTS

Determination of sulfur dioxide in roaster gases (STUER, CROB) (SANDER) 7.

Alkali metal cyanide. F. J. METZGER. U. S. 1,388,586, Aug. 23. In the manuf. of NaCN, the reaction zone of a retort is filled with a mixt. of Na_2CO_3 , C and Fe and a N-carrying gas is passed through the mixt. while it is tumbled and highly heated. The reaction can be carried out in a rotating inclined retort mounted within a furnace.

Aluminum sulfate. R. MOLDENKE. U. S. 1,388,436, Aug. 23. Finely powdered bauxite is mixed with an amt. of concd. H_2SO_4 equiv. to that which will combine with the available Al_2O_3 present and the mixt. is vigorously agitated at a temp. of about 280-315° in an atm. of acid vapors to form $Al_2(SO_4)_3$ in granular form. The latter is afterward mixed with sufficient H_2O to produce a cryst. sulfate.

Permanganates. J. R. MACMILLAN and J. L. K. SNYDER. U. S. 1,387,656,

Aug. 16. In the manuf. of NaMnO_4 , a manganate roast, such as is obtained by heating soda and Mn oxides, is treated with a soln. contg. some NaMnO_4 and the mixt. is chlorinated in order to form additional NaMnO_4 .

Potassium compounds from silicate rocks. S. MCKIRAHAN. U. S. 1,388,276, Aug. 23. KF is volatilized and recovered by heating feldspar, leucite, glauconite or similar K-bearing silicate rocks with fluorspar.

Furnace for manufacture of phosphorus and phosphoric acid. W. H. WAGGAMAN and T. B. TURLEY. U. S. 1,387,817, Aug. 16. The furnace comprises a shaft or charge chamber in which a charge of reacting materials such as phosphate rock, SiO_2 and coke is heated to a smelting temp. by means of fuel introduced. This smelting chamber discharges into a slag chamber which slopes from each end toward the center and is of greater length than width and which is narrower at its top than at the bottom and the material discharging from the shaft is maintained in molten condition by flame and hot blasts introduced into the slag chamber and playing above the slag. Volatilized reaction products including P and H_3PO_4 are withdrawn from the shaft and hearth and condensed and the exhausted slag is discharged from the hearth.

Reacting on carbides with nitrogen. J. H. REID. U. S. 1,388,603, Aug. 23. CaC_2 mixed with a gaseous catalyst such as HCl or CCl_4 is heated and reacted upon by N in order to form CaC_2N_2 . The presence of the catalyst lowers the reaction temp. required.

Electric oxidation of air or nitrogen. W. T. HOOFNAGLE. U. S. 1,388,112, Aug. 16. Air or a mixt. of N and O is passed through an elec. field and the products are immediately brought into contact with a catalyst, such as H_2O vapor, in order to fix the N oxides produced, in the form of acid.

Tube for nitrogen-fixation furnaces. F. J. METZGER. U. S. 1,387,505, Aug. 16. Furnace tubes adapted for use in the fixation of N by heating alkali metal compds. and C in the presence of N are formed of an outer shell of nichrome or other oxidation-resistant material with a lining of Fe or steel.

Metallic cement. F. P. WEST. U. S. 1,388,011, Aug. 16. A cement adapted for repairing broken pipes or castings is formed of Fe oxide 12, ZnO 1, PbO 1.5, comminuted Al 4 parts and water-glass soln. to form a pasty mixt.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Silica in 1920. L. M. BEACH. U. S. Geol. Survey. *Mineral Resources of U. S., 1920*, Part II, 151-2 (preprint No. 17, published Oct. 11, 1921). E. H.

The possibility of preparing high-grade silica bricks from quartzite rock. E. Lux. *Stahl u. Eisen* 41, 258-64 (1921).—Good silica brick can be made from quartzite rock provided a sufficiently high burning temp. is used. R. S. DEAN

Note on the effect of firing temperatures on the strength of fireclay and stoneware bodies. H. G. SCHURECHT. *J. Am. Ceram. Soc.* 4, 366-74 (1921).—Four clays were studied as to cross breaking strength, porosity, and shrinkage after firing to different temps. Apparently clays of this general type develop maximum strength on firing to cone 8 even though porosity and shrinkage data show the bodies to be under- or over-fired at this temp. Bodies which develop max. shrinkage and minimum porosity at cone 8 have a greater ratio of fired strength to dry strength when fired to cone 8 than those bodies which are under- or over-fired at cone 8. C. H. KERR

The water smoking of clays. R. F. GELLER. *J. Am. Ceram. Soc.* 4, 375-89 (1921).—Two plastic brick clays, 1 shale and 1 fireclay were studied; 4-in. cubical test

specimens were used. To save time in water smoking, the ware should first be well dried at 100° with good circulation in the kiln. Even heavy clay products should be water smoked in 15 hrs. with a heating rate of 20° per hr. C. H. KERR

National review of the sagger situation. GEORGE SIMCOE. *J. Am. Ceram. Soc.* 4, 393–406(1921).—A list of 25 questions was submitted to a large number of makers of clay products with the following resultant information: (1) SiC and Na silicate are in common use; (2) a sagger with 30% SiC is economical if it lasts 20 or more fires; (3) jaw crusher is better than pan grog; (4) costs are usually unknown and better cost accounting is urged. The answers are fully tabulated. C. H. KERR

Feldspar. ARTHUR S. WATTS. *Mineral Ind.* 29, 226–7(1920).—Production figures and a list of grinding mills are given. A. BUTTS

Abrasives. J. VOLNEY LEWIS. *Mineral Ind.* 29, 1–9(1920).—An account of the production of emery, corundum, and other abrasives, with statistics and a bibliography. A. BUTTS

Garnet. D. H. NEWLAND. *Mineral Ind.* 29, 10–1(1920).—A discussion of the sources, use, market and production of abrasive garnet. A. BUTTS

Nickel oxide in glazes. J. D. WHITMER. *J. Am. Ceram. Soc.* 4, 357–65(1921).—Conclusions drawn from an empirical study: (1) ZnO tends to produce blue colors with NiO; (2) ZnO is not essential in producing grays with NiO but may be present in amounts up to 0.3 equiv.; (3) BaO with CaO and K₂O gives browns and with ZnO, purples, reddish purples and reds when used in proper proportions; (4) BaO is not essential in producing grays but may partly replace CaO; (5) CaO with ZnO produces blues and must be present with MgO to produce grays; (6) MgO tends to produce grayish tints when used with other oxides. To produce neutral grays MgO should be used with CaO or with CaO and BaO. Bluish tones of gray result when ZnO is present; (7) the coloring influence of K₂O is slight but it promotes maturity and good surface. C. H. KERR

Refractories for oil-fired furnaces and boilers. W. H. GRANT. *J. Am. Ceram. Soc.* 4, 390–2(1921).—Failure results from (1) spalling and falling of the side wall bricks, (2) disintegration of bricks hit by the flame, (3) glazing and resultant penetration and weakening by the glaze, (4) erosion by the flame. C. H. KERR

Note on the acid-resistance of enameled cooking utensils. B. T. SWENLY. *J. Am. Ceram. Soc.* 4, 407–12(1921).—Expts. indicated that the surface which is uppermost during firing is the more readily attacked but discussion showed that the differences were more likely due to the nature of the furnace gases or to volatilization. C. H. KERR

Some data on the composition of arsenic enamels for copper. B. T. SWENLY. *J. Am. Ceram. Soc.* 4, 350–6(1921).—With 0.1 equiv. As₂O₃ in a Cu enamel applied dry, the following relations hold: (1) increase in SiO₂ increases the tendency to fracture, increases refractoriness, does not affect opacity or luster; (2) increase in B₂O₃ above 0.2 equiv. causes mattness and decreases the tendency to fracture; (3) increase in K₂O at the expense of PbO causes better flowing, maturity at a lower temp., greater solubility, decreased tendency to fracture and with more than 0.6 KNaO the enamel matures to a clear glass; (4) high-PbO enamels are very opaque, do not flow well and attack the Cu excessively. Limits in compn. of this type of enamel are given as: KNaO, 0.3 to 0.7; PbO, 0.7 to 0.3; SiO₂, 1.3 to 1.8; B₂O₃, 0.0 to 0.2; As₂O₃, 0.05 to 0.15. C. H. KERR

Abrasive for grinding and smoothing glass. W. L. KANN. U. S. 1,387,649, Aug. 16. Glass is ground and smoothed preparatory to polishing by the action of particles of cryst. garnet or similar abrasive material which is broken down into successively smaller and smaller cryst. particles during the grinding and smoothing operations.

Flameless combustion furnace. M. MATHY. U. S. 1,388,355, Aug. 23. Furnaces adapted for heating glass in crucibles are formed with one or more walls consisting of

boxes of refractory plates contg. porous refractory material in the heart of which flameless combustion of gases is maintained.

Rendering furnace walls impervious to gases. C. M. SHIPMAN. U. S. 1,387,739, Aug. 16. Furnace walls are rendered impervious to the passage of hot combustion gases by treating the walls with a slurry formed of clay, SiO₂ and sol. silicate and then exposing the treated walls to hot combustion gases.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Cement. ROBERT W. LESLEY. *Mineral Ind.* 29, 74-87(1920).—A review of the cement industry in the U. S. and foreign countries, giving statistics and notes on technology. A. BUTTS

Cement in 1919. ERNEST F. BURCHARD. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 387-401(preprint No. 30, published Sept. 21, 1921). E. H.

Interpreting the chemical analysis of portland cement. J. C. WITT. *Eng. News-Record* 87, 650-2(1921).—The limitations of chem. analysis in testing portland cement are discussed. The relative amts. of the several components cannot be detd. directly, and indirect analysis involves so many sources of errors that the results are not dependable. Since the relation between the compn. and physical behavior of cement is not fully understood, physical tests are indispensable. J. C. W.

The destruction of cement and of concrete conduits and masonry for sewage canals, reservoirs and similar works, and suitable means of prevention. A. SPITZGERER. Mannheim. *Z. Wasserversorgung Abwasserwissenschaft* 7, 46-8, 51-5, 63-5(1920).—Both cements and concretes are easily destroyed by various agents. These agents are classed according as they occur in (1) the ground underlying the works; (2) the liquid conducted or held; (3) the surrounding air and (4) the materials used as ingredients in the cement or concrete. In (1) and (2) are acids and acid salts, chiefly those giving an acid reaction with Congo red, methyl orange or rosolic acid, but occasionally those neutral to these indicators; any S compnd., especially H₂S, sulfates, sulfites, thiosulfates and sulfides; nitrates; H₂O contg. CO₂; Mg compds.; Na and K salts and saponifiable fats and oils. In (3) are chiefly H₂S and CO₂. In (4) are most frequently CaSO₄ and Mg compds. Together with these agents are incidental effects such as elec. energy and mechanical vibration. According to Endell the most injurious effects are from H₂O contg. sulfates of all kinds and humus waters from marshy soil. Upon the class and character of the injurious agent depend the possibility and method of protection. Cements and concretes resistant to the agents are classed as those (1) mixed without a flux; (2) with a preventive chem. compnd. incorporated in the mix; (3) with an insol. org. compnd. incorporated in the cement or concrete to prevent porosity, and (4) with a superficial impregnation of a resistant substance to prevent microporosity. To (1) belong cements and concretes without a flux which reacts with the external injurious compnd. Trass and puzzolana are the commonest substances added to increase resistance in (2). (3) includes certain soaps, fats and oils incorporated in the mix. (4) includes Mg, Si and Al fluorides, tars and asphalts. Compds. which are seldom concerned but which attack cements are (NH₄)₂CO₃, C₆H₅(OH)₂, sugar, NH₃ and Pb and Zn compds. Besides the agents mentioned, the mollusks, *Teredo navalis*, *Lithodomus (Lithophagus)* and *Pholas dactylus* destroy cements. The articles are replete with references to previous investigators but without the sources. S. asserts however that complete references in the literature will be furnished on application. C. C. DAVIS

Cement tile. M. CHARPENTIER. *Rev. Mat. Constr. Trav. Pub.* No. 139, 63-6, No. 140, 87-9(1921).—Composition: Artificial cement 22.3-24.2%, washed sand

(3 mm. screened) 67.1-69.7% color oxides 0.5, H₂O 7.5-8.2%. Such tile have fair resistance to compression, are interchangeable, impermeable to H₂O, non-porous, withstand freezing and rapid heat treatments, hold body and glaze color well, and look like terra cotta, in place of which they may be used.

LOUIS NAVIAS

Gypsum. FRANK A. WILDNER. *Mineral Ind.* 29, 340-8(1920).—1920 was a record year in all branches of the gypsum industry. Agricultural gypsum increased 270%.

A. BUTTS

Lime in 1919. G. F. LOUGHLIN AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 405-18(preprint No. 31, published Oct. 6, 1921).

E. H.

Slate in 1920. G. F. LOUGHLIN AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 135-43(preprint No. 15, published Oct. 12, 1921).

E. II.

Stone in 1919. G. F. LOUGHLIN AND A. T. COONS. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Part II, 419-55(preprint No. 32, published Oct. 18, 1921).

E. H.

Magnesium oxychloride cement. J. L. TURFS. U. S. 1,386,914, Aug. 9. A cement material is produced by agitating calcined magnesite in a closed vessel while introducing into the material sufficient HCl gas and H₂O vapor to produce a product in the proportions of 5 MgO, 1 MgCl, 5 H₂O.

Mixture for making bricks. J. SMITH. U. S. 1,385,757, July 26. A mixt. for brick making is formed of cement, coal ashes and brick dust in about equal amts.

Oil-proofing concrete tanks. C. ELLIS. U. S. 1,385,941, July 26. Concrete tanks are rendered oil-proof by treatment with an acid soln. of sulfite cellulose waste liquor which is allowed to react with alkali of the concrete.

Tarry paving material. C. HONDA. U. S. 1,386,932, Aug. 9. See Brit. 151,852 (C. A. 15, 742).

Roofing material. H. F. WEISS. U. S. 1,387,219, Aug. 9. A roofing is formed by mixing dry solid fibrous material and binder such as wood fiber and pitch or asphalt, compressing the mixt. and then spraying it with coal-tar pitch, asphalt or other water-proofing substance.

Laminated-wall receptacles. R. P. PERRY. U. S. 1,386,278, Aug. 2. A layer of moldable material such as paper-stock contg. some pitch or asphalt is formed upon a porous carrier, e. g., a perforated mold, and is then united with a second layer of material contg. more waterproofing substance, with or without a bituminous or non-adhesive lining or coating.

Building felt. R. P. PERRY. U. S. 1,386,277, Aug. 2. Sheets of porous building felt are made containing rounded particles of pitch, rosin, wax or similar waterproofing material too large to pass through a 100-mesh screen.

Preserving wood. A. C. CHANDLER. U. S. 1,388,513, Aug. 23. Wood is preserved by impregnating it with a soln. of Cu carbonate in Na₂CO₃ and H₂O and then allowing the Cu carbonate to ppt. in the wood.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Coal and coke. FRANK H. KNEELAND. *Mineral Ind.* 29, 93-138(1920).—A review of the coal industry, dealing with production, distribution, prices, stocks, etc., in the U. S., the world's production, and output and conditions in foreign countries. Coke and by-products are included.

A. BUTTS

The utilization of wood constituents for fuel. CARL G. SCHWALBE. *Eberswalde Brennstoff Chem.* 2, 276-81(1921).—Review of the problem of wood-waste utilization, especially the formation of humus-like substances during wet distn., hydrolysis with dil. or concd. acids and fermentation of the sugars, and utilization of alk. or acid waste liquors from pulp mills. W. B. V.

Risks in handling and storing coal, oil and by-products. C. E. PAIGE. *Am. Gas. J.* 115, 315-6, 326-7(1921).—The subject is treated from a fire standpoint.

J. L. WILEY

Froth flotation as applied to the preparation of coal for coking and briquetting. E. EPSER. *Iron & Coal Trades Rev.* 103, 473-4(1921).—E. explains the scientific principles upon which the process is based and mentions some of its com. applications. Coals contg. 30-40% of impurities can be purified to 4-5%, the coal thus obtained being excellent for making metallurgical coke which is tough, hard and forms not more than 2% of breeze. Flotation offers a considerable help toward the soln. of the problem of fuel economy. J. L. WILEY

Alcohol as a combustion fuel. E. C. FREELAND AND W. S. HARVEY. *Sugar* 23, 432-4, 474-6, 536-8(1921).—A general discussion of the uses of alc. as a motor fuel.

C. H. CHRISTMAN

Gaseous fuel in the shipbuilding yard. GEO. KRELLER. *Iron and Coal Trades Rev.* 103, 476-8(1921); *Gas World* 75, 269-71(1921).—The use of gas for annealing, hardening, billet and rivet heating, core and mold drying, and nut and bolt forging is discussed, and the advantages over other kinds of fuel are given. J. L. WILEY

Gas producers for bituminous coal. HENRY W. SELDON. *Blast Furnace & Steel Plant* 9, 586-7(1921).—An outline of the points to be observed in choosing a producer and in operating to obtain the best results. J. L. WILEY

Ascension pipe developments. W. H. WARREN. *Gas World* 75, 245-9(1921); *Gas. J.* 155, 723-8(1921).—An installation of the Congdon ascension pipe system at Beckton and a modification of it are described. (Cf. *C. A.* 15, 2539.) In comparison with other types, the NH₃ results are improved, the oils in the tars are superior to those in the tar in the ordinary hydraulic main, and the gas is better, 585 B. t. u. and 504 B. t. u., the iovers being 9.54 and 20.27% resp. J. L. WILEY

Determination of sulfur in "Gasmasse" (FLEISCHER) 7. Petroleum and natural gas (DAY) 22. A further application of diagrams for waste-gas analysis (KUTZNER) 7. Power gas from sewage (WATSON) 14. Progress in ore dressing and coal washing in 1920 (RICHARDS, LOCKE) 9. Chemical industry power and fuel data (GOOWIN) 13.

Motor fuel. E. W. STEVENS. U. S. 1,388,531, Aug. 23. A fuel mixt. for use as a gasoline substitute is formed of kerosene or similar material 50, EtOH 30, Et-Me ether 5-10 and toluene 8-10 parts.

Producing gas from coal or other solid fuel. F. G. C. RINCKER. U. S. 1,388,145, Aug. 16. Water gas is passed through coal or the like so as to form gases and leave a coke residue and steam is then passed through the coke residue before it has substantially cooled to produce water gas and the latter is passed while hot through another mass of fuel which is at a lower temp. than the water gas acting on it. The mixt. of water gas and distd. gases thus formed is led directly to a receiver. Cf. *C. A.* 14, 2077.

Producer gas. A. H. LYNN. U. S. 1,388,052, Aug. 16. Hot products of combustion from furnace plants fired with producer gas are passed into direct contact with H₂O to heat the latter at atm. pressure and the heated H₂O is circulated in contact with air to heat and sat. the latter with moisture. The air, thus heated and moistened, is passed into a gas producer which supplies gas to the furnace plant and the H₂O is reused for heating and satg. air for supply to the producer.

Recovering values from exhaust gases of internal-combustion engines. A. J. PARIS, JR. U. S. 1,388,490, Aug. 23. Exhaust gases are treated with a heat-absorbing agent such as kerosene and are then cooled to condense and sep. products such as HOAc and cracked hydrocarbons.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Petroleum and natural gas. DAVID T. DAY. *Mineral Ind.* 29, 499–530(1920).—Statistical review and discussion of the world's industry. A. BUTTS

Colloid chemistry of petroleum. F. W. PADGETT. *Chem. Met. Eng.* 25, 189–92 (1921).—A discussion of problems of petroleum technology, including crude-oil emulsions, used lubricating oils, emulsifying oils, greases, crystn. of paraffin wax, and filtration through fuller's earth, all treated from the standpoint of colloid chemistry. M. R. SCHMIDT

Asphalt. ANON. *Mineral Ind.* 29, 50–7(1920).—Statistical review. A. BUTTS
Effect of chemical reagents on the microstructure of wood. ALLEN ABRAMS. *J. Ind. Eng. Chem.* 13, 786–90(1921). Correction. *Ibid.* 13, 960.—Sections of wood (20–40 μ in thickness) were subjected to the action of various electrolytes by a new procedure, and the changes observed by means of the microscope. Typical expts. are described and discussed and shown by photomicrographs. Measurements on treated and untreated sections are compared. Cellulose solvents act strongly on both the middle lamella and on the cell wall. Oxidizing agents act on the cell wall but have little effect on the middle lamella. Pulp-making materials appear to affect the middle lamella strongly, but have less effect on the cell wall. LOUIS E. WISE

Hardwood-distillation industry. L. F. HAWLEY. *Chem. Met. Eng.* 25, 137–40, 195–9, 237–41(1921).—A comprehensive descriptive article, with frequent references, outlining the importance of distn. products in the industry, development of the industry, retorts, kilns, and ovens, methods of drying wood prior to distn., relation between compn. of wood and its distn. products, relation between temp. and the decompn. of wood substance, temp. control, influence of speed of distn., use of precipitators for the sepn. of fog in wood gas, products obtained from wood tar and their uses, etc. No new data are presented but H. has corrected a number of errors that have crept into the literature on wood distn. So-called chem. methods are not used commercially for the sepn. of acetone and methanol. Klason's work on the effect of temp. on decompn. of wood is reliable, whereas the data contained in Violette's tables are incorrect and misleading.

LOUIS E. WISE

Turpentine, methanol, acetone and tar from stump wood. LINK. *Chem. Ztg.* 45, 820(1921).—The assertion that turpentine cannot be produced commercially directly from stump wood is denied by L. Turpentine can first be removed by steam distn. and the residue subjected to destructive distn. A plant in Wolbyniem gave an av. yield per cu. m. of stacked wood during 4 years of operation: 9.25 kg. grade Ia turpentine, 0.89 kg. grade IIa turpentine (Kienol), 61.3 kg. pine tar, 10.0 kg. 80–82% acetate of lime, 1.25 kg. pure methanol, and 72.6 kg. wood charcoal. LOUIS E. WISE

The vacuum distillation of wood. OSSIAN ASCHAN. Helsingfors. *Brennstoff Chem.* 2, 273–6(1921).—Preliminary expts. failed to show any evidence of fusion of the wood substance at temps. up to 290–310°, where sintering begins. Distn. of dry birch sawdust at temps. below 400° under pressure of 6–8 mm. gave the following products: AcOH 6.7, HCOOH 0.6, hydrocarbons, phenol ethers, etc. 4.9, phenols 15.2, charcoal 35.3, water, gases, etc., 27.6%. No appreciable quantities of MeOH or MeCO were formed. The high yield of charcoal is the only result of technical interest. The frac-

tion of the distillate b. 130-140° contained a small quantity of a yellowish cryst. substance which was odorless, sol. in Et₂O and glacial AcOH, difficultly sol. in EtOH and MeOH, insol. in Na₂CO₃ or NaOH; when crystd. from MeOH it m. at 48°; when ptd. from MeOH by diln. it m. at 51-53°. W. B. V.

Problems in the improvement of hydrocarbons (KORTSCHAU) 10.

Purifying hydrocarbon oils. C. I. ROBINSON. U. S. 1,387,868, Aug. 16. Petroleum oils, after treatment with H₂SO₄, to effect their purification, are mixed with 20% of a 45% aq. soln. of isopropyl alc. to dissolve sulfonated compds. from the oil and the isopropyl alc. soln. is sepd. from the purified oil, while slightly heated.

Purifying hydrocarbon oils. E. B. COBB. U. S. 1,387,835, Aug. 16. Hydrocarbon oils such as heavy petroleum distillates are treated with concd. H₂SO₄. Oil-sol. sulfonated compds. are removed from the oil by steam distn. of most of the oil from them and the oil is again treated with strong H₂SO₄ and washed with isopropyl alc., which serves to remove residual sulfonation derivs. Oils thus treated are suitable for medicinal use.

Cracking hydrocarbon oils. J. W. COAST, JR. U. S. 1,388,629, Aug. 23. Oil of relatively low b. p., such as kerosene, is passed through a cracking coil into a cracking still contg. oil of higher b. p. such as gas oil or fuel oil and the app. used is so regulated and heated that the low boiling oil treated is subjected to higher temp. and pressure than the oil of higher b. p.

Cracking petroleum hydrocarbons. E. M. CLARK. U. S. 1,388,514, Aug. 23. In distn. of hydrocarbon oils under pressure in a cracking still, fresh stock is introduced into the pipe leading from the still to the condenser and allowed to flow into the still in counter-current to the vapors. This mode of operation serves to increase the yield of light products and the capacity and efficiency of the still.

Decolorizing viscous hydrocarbon oils. E. B. COBB. U. S. 1,388,517, Aug. 23. Hydrocarbon oil which has a viscosity of over 40 sec. at 38° is treated with H₂SO₄ and the acid sludge which is formed is removed. The oil is distd. with dry steam to obtain a viscous distillate without decompn., the distillate is purified with H₂SO₄ and the oil is then filtered through decolorizing material such as Florida clay. Products thus prepd. are suitable for medicinal use.

Viscous petroleum oil mixture. E. B. COBB. U. S. 1,388,832, Aug. 23. The pat. relates to blending viscous mineral oils from different sources to form a stock suitable for medicinal use when decolorized.

Lowering the boiling and flash points of kerosene. W. M. WHEELER. U. S. 1,387,876, Aug. 16. Kerosene or similar oil is vaporized, and the vapor is mixed with steam. The mixt. is permitted to pass through a mass of broken fire brick in an expansion chamber under low pressure, under gradually increasing temp. (which may reach as high as 430°) and the vapors are then permitted further to expand; they are then heated to a higher temp. (preferably about 480°) at atm. pressure and are condensed and subjected to gravity sepn.

Apparatus for cracking petroleum oils. C. EXSTRAND. U. S. 1,388,415, Aug. 23. The app. is adapted for cracking or distg. petroleum oils and comprises a retort through which the oil is forced under pressure and an expansion and mixing chamber with baffle plates, against which vapors from the retort are forced through nozzles.

Superposed horizontal retorts for distillation of oil from shale or sand. J. B. JENSON. U. S. 1,388,718, Aug. 23. Material is fed successively through the retorts by screw conveyors.

23—CELLULOSE AND PAPER

A. D. LITTLE

Cellulose and sulfite pulp. A. KLEIN. *Paper Trade J.* 73, No. 10, 44-6, 52(1921).—A review of the various formulas for cellulose which have been proposed. Sulfite pulp or sulfite cellulose is in fact only a cellulose-rich residue of the decompr. of wood.

H. H. HARRISON

Chemical constitution of soda and sulfate pulps from coniferous woods and their bleaching qualities. SIDNEY D. WELLS. Forest Products Lab. *J. Ind. Eng. Chem.* 13, 936-9(1921).—Chem. characteristics of soda and sulfate pulps indicate that they are a very pure form of wood cellulose and capable of high yields of white fibrous and resistant materials. The sulfate process is much more efficient than the soda process in yielding a bleachable pulp from coniferous woods. The coloring matter in pulps is of the nature of a dye and can be removed without materially reducing the yields. Most of the action in cooking to reduce bleach consumption is to dissolve and degrade the cellulose. Modifications in bleaching methods give promise of greater results than modifying cooking methods. Modifications in which the bleaching operation was divided into two steps, with washing between steps, cut the bleach requirements in two. Pulps of better quality, both from physical and chemical considerations, are obtained by cooking the wood as little as possible in isolating the fibers and by accomplishing as much of the burden of purification in the bleaching and washing operations. C. J. WEST

Bleaching of sulfite pulp. B. M. PETRIE. *Paper Trade J.* 72, No. 24, 51; *Paper Industry*, 3, 430-1(1921).—Factors affecting bleaching favorably are strong cooking acid, properly cooked pulp, thorough washing, proper addition of bleach, proper temp. control during bleaching and uniformity of the unbleached pulp. Two gals. 5° Bé. hleach liquor per lb. of 35% bleaching powder is considered good mill practice.

H. H. HARRISON

Cooking of sulfite pulp. BENJAMIN T. LARRABEE. *Paper Trade J.* 72, No. 24, 38-9(1921).—For the manuf. of sulfite for book paper L. recommends the use of an acid having 6% total SO₃, 4.90% free and 1.10% combined SO₃. The pressure used and the time taken to come to pressure depend upon the moisture in the wood and the kind of wood. 290° F. is regarded as the desirable max. and 300° F. should not be exceeded.

H. H. HARRISON

Sulfite digesters for direct cooking. HARRY E. WESTON. *Paper Industry* 3, 829-32(1921).—A description of the digesters used in present practice. H. H. H.

Testing of wood pulp shipments for content of air-dry pulp. EMERSON LAB. *Paper Industry* 3, 563-7; *Pulp & Paper Mag. Can.* 19, 757-60(1921).—Description of the methods used for sampling pulp shipped in various forms. H. H. HARRISON

Groundwood preservation tests. JOHN S. BATES. *Pulp & Paper Mag. Can.* 19, 851-3(1921).—NaF was satisfactory as a preservative for groundwood pulp. It preserved the original color and quality and was comparatively inexpensive. 0.581% NaF on the wt. of the air-dry pulp was sufficient.

H. H. HARRISON

Camphor substitutes in the manufacture of celluloid. ALBERT PARSONS SACHS AND OSCAR BYRON. New York. *J. Ind. Eng. Chem.* 13, 893-901(1921).—A general article, discussing the manuf., properties and disadvantages of celluloid and the possible camphor substitutes, such as phosphoric esters, triphenyl phosphate, tritolyl phosphate, triacetin, ethylacetamide, etc. Patents covering camphor substitutes are listed by countries. C. J. WEST

Manufacture of copying and carbon papers. BRUNO WALThER. Berlin. *Chem-Ztg.* 45, 287-8(1921).—Discussion of the materials used in coating copying, tracing and carbon papers. C. J. WEST

The manufacture of paper pulp by means of chlorine. UMBERTO POMILIO. *Chimie & industrie* 6, 267-75(1921).—Paper pulp can be prep'd. from vegetable materials by treatment with NaOH, bisulfites, or oxidizing agents and then alkali. The last is the most efficient, and is used in the lab. for the detn. of cellulose; but it has not been extensively applied commercially on account of its high cost. In 1916 an Italian firm built a mill to make pulp according to the Cataldi patent (*C. A.* 11, 209). It has now been in operation for 4 yrs. and has shown that theoretical yields can be obtained on a com. scale, and that the quality of the pulp is superior to that of soda pulp. The "Elettrochimica Pomilio" is erecting a 10-t. mill to prep. *hemp pulp* by this process. Its advantages are simplicity, ease of control, low consumption of chemicals and raw materials, reduced labor, low power consumption, simple and compact equipment, and high yield. It also furnishes a ready market for surplus Cl production. A. P.-C.

Wood waste in paper making. C. J. WEST. *Paper Trade J.* 73, No. 10, 52(1921).—It is estd. that the total quantity of waste converted into pulp is 200,000 cords per annum. Sawdust has found use in the manuf. of board and has been made into satisfactory newsprint. H. H. HARRISON

Typha fibers in paper making. FR. RUEHLERMAN. *Paper Trade J.* 73, No. 7, 48-52(1921).—Photomicrographs of papers made from typha fibers in 1770. H. H. HARRISON

The cooking of plants for the preparation of paper pulp: cooking under pressure and without pressure. RAYMOND FOURNIER. *Papier* 24, 404-10(1921).—Under no conditions does treatment with alk. liquor alone give a pure cellulose; its action must be completed by an oxidizing treatment (generally called bleaching). Cooking under high pressure has a few advantages and many disadvantages. Results are given of tests carried out on wheat straw, reeds, papyrus and esparto, cooking at high pressure and without pressure under varying conditions being compared. F. concludes that the use of pressure presents no great advantage, and it should be supplemented by a mechanical treatment which allows of more intimate contact of the liquor with the material. When this was done and sufficient NaOH was used, the incrustants were solubilized in a fairly short time; but continuing the treatment for a long period (up to 700%) after this did not appreciably lower the yield; this shows that the cellulose was not attacked. The use of a large excess of NaOH does not greatly lower the yield. A. P.-C.

Paper-machine wires. V. BOUYER. *Papeterie* 43, 773-8, 818-26, 866-81(1921).—A detailed description of the different weaves of wire cloth used on paper machines, of their manuf., of the kind of work best suited for the various kinds of wires, and of the causes of deterioration. A. P.-C.

The effect of humidity on the moisture content of paper. ROSS CAMPBELL. *Paper Trade J.* 73, No. 2, 30-4(1921).—The result of lab. expts. has proved conclusively that the moisture content of paper is independent of the furnish and kind of paper, is a function of the relative humidity of the air in which the paper is, and is independent of the method of test. H. H. HARRISON

Analysis of cardboard: bulk and calendering. R. ISNARD. *Paper Trade J.* 73, No. 12, 44-6(1921).—See *C. A.* 15, 1214. H. H. HARRISON

Dyeing paper pulp. ANON. *Paper Trade J.* 73, No. 12, 42(1921).—Expts. show that it is better to add rosin size after the dye soln. than before and that the addition of a small amt. of NaHCO₃ is advantageous. H. H. HARRISON

Beating. C. C. STEWART. *Paper Trade J.* 72, No. 24, 30(1921).—Data are given showing that the effect of beating is independent of the consistency of the stock in the beater. H. H. HARRISON

Beating, sizing and loading. GEORGE TEREN. *Paper Industry* 3, 710-3(1921).—A description of the operations carried on in the beater. Retention figures for fillers in

paper are talc 82%, agalite 75%, clay 70%. Tabulated data of the retention of crown filler are given.

H. H. HARRISON

The development of suction rolls. WILLIAM MILLSPAUGH. *Paper Trade J.* 72, No. 24, 22-5(1921).—A discussion of the benefits to be derived from use of suction rolls.

H. H. HARRISON

Coating and fireproofing fabrics (U. S. pats. 1,388,824-9) 25.

Felt paper or felt. G. R. WYMAN. U. S. 1,388,685, Aug. 23. Mechanical features of manuf.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Production of explosives in the United States during 1920 with notes on mine accidents due to explosives. WILLIAM W. ADAMS. Bur. Mines, *Techn. Paper* 291, 44 pp.(1921).

E. H.

Researches on modern brisant nitro explosives. C. F. VAN DUIN AND B. C. ROSTERS VAN LENNEP. Nat. Research Council. *Reprint and Circ. Series* No. 15, 35 pp.(1921).—See *C. A.* 14, 2708.

E. H.

Munitions works explosion. ANON. *Chem. Age* (London) 5, 158-9(1921).—This reports one stage in the litigation growing out of an explosion, Sept. 1916, at the Range Works, Rainham, Essex, where *picric acid* was manufactured from *dinitrophenol* and $NaNO_3$ under the process invented by David Maron and George Wyss.

C. E. M.

Great German chemical works explosion. ANON. *Chem. Age* (London) 5, 370(1921).—A serious explosion occurred at the Oppau factory of the Badische Co. on Sept. 21 resulting in casualties estd. at 1000 killed and 1500 wounded, the destruction of the works, and severe damage to Mannheim, Ludwigshafen and other near-by towns, while its effects were noted at Frankfurt 37 miles distant. Apparently there was a series of explosions, the first occurring in one of the labs., two gas holders alongside being exploded, producing a crater 400 ft. in diam. and 100 ft. deep, and a warehouse contg. 200 tons of NH_4 compds. The directors state that such rigid precautions were taken prior to the prepn. and storage of these products that they believed all danger of explosion to be excluded. A description is given of the Oppau plant, its history and activity, with a detailed plan of the plant. The plant covered about 2000 acres, operated the Haber synthetic NH_3 process with the conversion of its products into other N compds., employed 5000 persons and cost 300,000,000 M. The material damage is estd. at 150,000,000 M.

CHARLES E. MUNROE

Security in handling inflammable liquids. ANON. *Chem. Age* (London) 5, 372(1921).—Describes, with drawing, a storage tank for petrol and other inflammable liquids, designed to store the liquid under atm. pressure, *protected by inert gases*, to dis tribute it pneumatically and to avoid any contact with the outside air.

C. E. M.

The North Western elevator explosion. DAVID J. PRICE AND HYLTON R. BROWN. *Am. Elevator and Grain Trade* 40, 179-96(1921).—This grain elevator was built of reinforced concrete with 182 bins 21 ft. 11 in. diam., 105 ft. deep and walls 7 in. thick, and 156 interstice bins. It was destroyed by a series of dust explosions through which 16 of the bins in the S. W. corner were completely blown out and the wrecking extended throughout the storage section and to the accessory buildings. The shock was distinctly felt 50 miles distant and the report heard 100 miles away. The origin was located in a fire in or near one of the grain dryers and the transmission of flames and of explosion waves was promoted by the tunnels existing under the storage section. Many recommendations are made; among them is the construction of thin walls on heavy frame

work by which the extent of damage inflicted by an explosion is limited. Much stress is also laid upon the importance of removing the dust which the elevator operator receives with the grain and which constitutes the menace to life and property, but regulations to this effect should include a provision for reimbursing the shipper for this shrinkage. It is this economic factor which has prevented the removal of dust from grain before storage from becoming established practice. The article is well illustrated; the "Chart of the Explosion" showing the means by which the point at which explosion originated was detd. is of special interest and importance. CHARLES E. MUNROE

Nitrostarch explosive. C. E. WALLER. U. S. 1,386,478, Aug. 2. An explosive of high brisance is formed of nitrostarch 60-70, NH_4NO_3 19-9, $\text{Ca}(\text{NO}_3)_2$, 4-8 and H_2O 17-13%.

Nitrostarch explosive. W. O. SNELLING. U. S. 1,386,437, Aug. 2. Deliquescent salts such as NH_4NO_3 are used in nitrostarch explosives together with sufficient H_2O to hold a substantial portion of the salt in soln., in order to reduce the sensitivity to shock or friction.

Explosives. W. O. SNELLING. U. S. 1,386,438, Aug. 2. H_2O in excess of 3% together with CdO , $\text{Ca}(\text{OH})_2$, ZnO or Zo(OH)_2 , 3-4% is present in explosives mainly formed of nitrostarch and NH_4NO_3 . The H_2O and hydroxide serve to reduce sensitivity to blows or friction. The proportions of the ingredients of the explosive may be nitrostarch 20-60, NH_4NO_3 60-20, H_2O 3-15 and ZnO 1-5%.

Preparing explosives from undried organic nitrates. W. O. SNELLING. U. S. 1,386,439, Aug. 2. H_2O present in undried org. nitrates such as nitrostarch is displaced by a concd. soln. of NH_4NO_3 or other inorg. nitrate, which forms an explosive directly without evaporative drying.

Nitrostarch explosives. W. O. SNELLING. U. S. 1,386,440, Aug. 2. An oil such as lard oil, cottonseed oil or mineral oil is added to nitrostarch explosives, to the amt. of 2-17%, as a desensitizing agent.

Match compositions. MANUEL PRADO P. U. S. 1,387,999, Aug. 16. Frictionally ignitable match-head compns. are formed with a slight excess of alk. material to prevent development of free acid in the compn. A mixt. of this kind may, e. g., be formed from glue, sawdust, S, coal cinders, gluten, Sb sulfide, $\text{Ca}(\text{OH})_2$, charcoal, coke, brick powder, glass, $\text{K}_2\text{Cr}_2\text{O}_7$, KClO_3 and H_2O .

Torch fuse-lighter. E. P. AURAND. U. S. 1,388,502, Aug. 23. Gelatinized nitrostarch is employed as a binder for mealed black gunpowder or similar material for making fuse-lighting torches.

Binder for combustible materials. E. P. AURAND. U. S. 1,388,501, Aug. 23. A binder of gelatinized nitrostarch is used with combustible materials such as signal flare, rocket or colored-fire mixts.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The modern dyestuff industry. H. E. FIERZ. *J. Soc. Chem. Ind.* 40, 361-6R (1921); *Chem. Age* (N. Y.) 29, 411-3(1921). E. H.

The mechanism of dyeing. M. BADER. *Rev. textile et des chimistes coloristes* (Jan., Feh., 1921); *Industrie chimique* 8, 370.—The tinctorial power of dyestuffs is closely related to the presence of 4 constitutional groups: carbonyl, sulfo, ammonium, and oxonium. The sulfo and oxonium groups are very important as they give the direct silk and wool colors. Crystalloid dyes, which yield true solns., dye animal fibers directly but have no affinity for cotton. Insol. or highly colloidal dyestuffs have

no appreciable tinctorial power, and their application is limited to mechanical fixation by means of adhesives. The general principle for the utilization of azo colors consists in depositing the various constituents on the fibers and making them react there.

A. P. C.

Direct dyeing of wool. L. GUCLIALMELLI AND C. G. ESTRELLA. *Anal soc. quim. Argentina* 8, 325-6 (1920).—Wool and silk can be dyed directly by diazotization and subsequent treatment with certain polyphenols and phenolic glucosides. By the use of metallic salts, such as $K_2Cr_2O_7$ and $CuSO_4$, variations in shade and greater fastness to light can be obtained.

J. S. C. I.

Felt paper or felt (U. S. pat. 1,388,685) 23. Impregnating leather, cloth, etc., with cellulose nitrates (U. S. pat. 1,388,169) 29.

Dyes. G. DE MONTMOLLIN and H. J. SPIELER. U. S. 1,387,596, Aug. 16. Dyes adapted for use on wool in acid baths with subsequent chroming are formed by the reaction of a C tetrahalide upon an α -naphthol deriv. which is unsubstituted in its 4-position, in the presence of a catalyst and acid-fixing agent; e. g., by the interaction of $Na\ \alpha$ -naphtholate on CCl_4 in the presence of a catalyst such as Cu. Na α -naphthol-2-carboxylate yields a fast blue dye.

Diazoy dye. W. M. RALPH. U. S. 1,5182, Aug. 23. See original pat. 1,371,979, C. A. 15, 1816.

Apparatus for dyeing or bleaching fibers on bobbins or beam rollers. A. WIOLAND. U. S. 1,388,081, Aug. 16.

Coating and fireproofing fabrics. A. ARENT. U. S. 1,388,824, Aug. 23. Cloth for airplanes or other uses is coated and rendered fire-resistant by treatment with a soln. of varnish gum, gutta percha and $SbCl_3$ in CCl_4 and then with H_2O . U. S. 1,388,825 relates to a compn. for coating airplane wings or other fabrics prepd. by dissolving $SbCl_3$ in $AmOAc$ and mixing the soln. with nitrocellulose. U. S. 1,388,826 relates to a fire-resisting material for treating wood, paper or cloth formed of creosote 1 gal. and $SbCl_3$ 2 lbs. U. S. 1,388,827 relates to the addition of $SbCl_3$ to varnishes such as spar varnish and gutta percha to render them non-inflammable. U. S. 1,388,828 relates to waterproofing fibrous materials such as paper or canvas by a mixt. of linseed oil or other drying oil with $SbCl_3$ and a solvent such as $AmOAc$, or C_6H_6 . U. S. 1,388,829 relates to use of tarry substances with $SbCl_3$ for impregnating fibrous materials. Cf. C. A. 14, 1879.

Artificial silk. E. BRONNERT. U. S. 1,387,882, Aug. 16. A pptg. bath comprising $PhSO_2Na$ and H_2SO_4 (monohydrate) is employed in the production of artificial silk from viscose. This bath produces soft full-bodied threads.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

The constitution of smalt. A. DUBOIN. *Compt. rend.* 172, 972-4 (1921).—By the fusion of KF , KCl , SiO_2 and CoO , D. has prepd. a deep blue cryst. double silicate of Co and K, corresponding to the formula $K_2O \cdot CoO \cdot 3SiO_2$; also a light blue chlorosilicate of the compn. $KCl \cdot K_2O \cdot CoO \cdot 4SiO_2$. The latter product, which appears to be the principal constituent of smalt, was also prepd. by the action of SiO_2 on the double fluoride of Co and K in the presence of an excess of KCl .

C. B. E.

Detection and estimation of coal tar oils in turpentine. V. E. GROTLISCH AND W. C. SMITH. *J. Ind. Eng. Chem.* 13, 791-3 (1921).—Adulterated turpentine (100 cc.) is treated with HCl gas, the pinene-HCl filtered off, the filtrate concd. *in vacuo* and

sulfonated under carefully regulated conditions. The resulting mixt. on steam distn. yields any mineral oil originally present as adulterant. The acid residue when heated by Armstrong and Miller's method (*J. Chem. Soc.* 45, 150) yields coal-tar hydrocarbons in the distillate. Their vol. \times 2.2 = % coal-tar originally present in the turpentine. Methods for the further identification of adulterants are given. The method is not strictly applicable to wood turpentine.

LOUIS E. WISE

The composition of French turpentine. VEZES. *Compt. rend.* 172, 977-80 (1921).—A polarimetric method of analysis (cf. Darmois, *Thèse, Paris*, 1911, p. 53) has been used with satisfactory results for the detn. of the proportions of pinene and nopinene in turpentine. The procedure depends upon the different rotatory powers of these two isomeric components. Details of the application of the method are included.

C. B. E.

Effect of variation in analytical constants of linseed and soy-bean oils upon the quantitative determination of linseed oil in mixtures of the two oils by means of the iodine and hexabromide numbers of the fatty acids. EDWARD A. TSCHUDY. *J. Ind. Eng. Chem.* 13, 941-3 (1921).—From a study of the analytical values of linseed-soy oil mixts. reported by Bailey and Baldsiefen (*C. A.* 15, 603), T. develops equations representing the relations between per cent linseed oil, I nos., and hexabromide nos. These relations show that an estimate of the amount of linseed oil in such mixts. may differ from the actual per cent of linseed oil present, by +13% to -9% when the estimate is based on the hexabromide detn., and by +17% to -18% when based on the I detn.

F. A. WERTZ

Cellulose varnishes. L. CLÉMENT AND C. RIVIÈRE. *Chimie & industrie* 6, 283-95 (1921).—A general review of the prepn. and applications of various types of cellulose acetate and nitrocellulose varnishes, with a brief outline of a scheme of analysis of these varnishes.

A. P.-C.

Coating and fireproofing fabrics (U. S. pat. 1,388,824) 25.

Ship's-bottom paint. S. ASAOKAWA and K. NOSAWA. U. S. 1,387,448, Aug. 16. "Kwashi-pan" is used in submarine paints, together with varnish, oil and coloring matter.

Blanc fixe. G. MOORE. U. S. 1,388,285, Aug. 23. Blanc fixe is prep'd. by mixing finely divided crude barytes with NaCl and NaNO₃ or Na₂CO₃, fusing the mixt. and then chilling it by discharging it into cold H₂O.

Preventing offsetting of printing inks. R. L. FEARN, JR. U. S. 1,388,418, Aug. 23. Offsetting of ink on paper is prevented by heating the paper, subjecting it to the action of ozonized air and then reheating it.

27—FATS, FATTY OILS AND SOAPS

E. SCHERUBEL

Grape-seed oil. FRANK RABAK. *J. Ind. Eng. Chem.* 13, 919-21 (1921).—Domestic grape-seed oil from the Concord grape has some properties comparable with oils of foreign origin. The differences noted may be ascribed to conditions of growth, climate, soil, variety, and methods of extn. The approx. compn. is: linolein 53.59, olein 35.87, palmitin 5.23, stearin 2.26, unsaponifiable matter 1.61%. The remainder of the oil consists of small amts. of free fatty acids and volatile fatty acids. On account of its ease of extn. and refining the oil should find its most important use as an edible oil.

E. SCHERUBEL

Chemical investigation of mutton-bird oil. C. L. CARTER. *J. Soc. Chem. Ind.* 40,

220T(1921).—Mutton-bird oil is extd. from the stomach of a petrel, *Aestrelata lessoni*, peculiar to Australasia. When disturbed the bird ejects this oil from its nostrils. It is said that the oil serves as a food for the young birds. The consts. of the oil were: d_{16.5} 0.884, higher alcs. 38.4%, sapon. no. 119.6, I no. 130 Wijs, 108 Hübl, I no. of fatty acids 178 Wijs, 150 Hübl. The oil is non-drying. It deposits spermaceti at 6°. On sapon. with alc. KOH, 100 g. of oil gave 38.38 g. of alcs. (chiefly ethyl), 61.38 g. of mixed fatty acids and 3 g. of sol. coloring matter. A quant sepn. of the fatty acids by the Pb salt ether method gave 96.5% of acids of the oleic acid series and 3.5% of the stearic acid series. The oil should be of value as a lubricant and as a leather dressing, but the supplies are small.

E. SCHERUBL

Halphen's test improved. R. A. KUZVER. *J. Am. Pharm. Assoc.* 10, 391-5 (1921).—The official Halphen test for cottonseed oil in olive oil is unsatisfactory because S crystallizes from the C₆H₅OHCS₂ mixt., thus rendering the test less sensitive. Further, NaCl crystallizes from the brine bath and the temp. cannot be raised above 106°. K. uses a mixt. of pyridine 100, CS₂ 100 cc. and S 2 g. The S is dissolved by heating the mixt. in a reflux apparatus. A mineral oil bath which may be heated to 115° is substituted for the brine bath. The test is sensitive to 1% of cottonseed oil. The color produced with 1% of cottonseed oil is very stable, some tests having shown no change in color on keeping for several months.

L. E. WARREN

The utilization of the Argentine thistle. BRUNO REWALD. *Chem.-Ztg.* 45, 805 (1921).—Waste lands produce, per hectare, 1000 kg. of seed contg. 41-44% of an edible oil. The press cake contains 52.5% protein and is a valuable feed. T. G. PHILLIPS

"Sawdust soap." F. W. RAICY. U. S. 1,387,804, Aug. 16. A mixt. adapted for removing grease from the hands is formed of soap, sawdust, Na₂CO₃, H₂O and paraffin or beeswax, in paste form.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Colloidal chemistry in the sugar industry. JAR. DÍDEK. *Listy Cukrovar.* 39, 185-90, 193-6(1921); *Z. Zuckerind. Čechoslov. Rep.* 45, 251-3, 263-6, 275-8(1921).—The fundamental theories of colloidal chemistry concerning diffusion, pptn. and adsorption are reviewed at length. Diffusion, defecation, satn. and crystn. should all be investigated from the colloidal standpoint. In the refining of sugar the decolorization problem is to a great extent dependent on colloidal chemistry whether the decolorizing agent is boneblack or a vegetable carbon.

JOHN M. KRNO

Technical control in (German beet) raw sugar manufacture. HERZFIELD. *Z. Ver. deut. Zuckerind.* 71, 558-71(1921).—This address calls attention to the necessity of returning to the more thorough factory control methods of former yrs. and to the desirability of a system of mutual control.

F. W. ZERBAN

The analysis of dried sugar beets. V. SÁZAVSKY. *Listy Cukrovar.* 39, 313-5 (1921).—In the detn. of moisture 20 g. of the powdered sample are dried at 100° for 4 hrs. For the digestion 26.1 g. and 400 cc. of water are taken and a small amt. of Pb acetate is added. The mixt. is digested on a water bath at 80-5° for 30 mins. with occasional agitation. This is then cooled, filtered after 2 hrs. standing and polarized at 20° in a 200-mm. tube. For the detn. of total sugars, 50 cc. of the above soln. is inverted in the usual manner and the vol. completed to 100 cc. 50 cc. are pipeted into a 250-cc. flask, neutralized with powdered Na₂CO₃, completed to vol. and filtered. In 50 cc. of this soln. reducing sugars are detd. in the usual manner by boiling with 50 cc. of Fehling's soln. An appended table gives the invert-sugar content, from which the

total sugars as sucrose are calcd. by use of the factor 0.95. Bruhn's method for the detn. of total sugars is recommended also. The invert sugar is detd. in the original digestion soln. by Fehling's soln., either gravimetrically or by titration according to Bruhns.

JOHN M. KRNO

Use of invertase for sucrose estimation. T. SWANN HARDING. Digestive Ferments Co. *Sugar* 23, 546-7(1921).—Errors in acid hydrolysis of sucrose by the Clerget method include the hydrolysis of other sugars present and the effect of the acidity upon optical non-sugars. Using invertase, no effect is found upon compds. present other than sucrose. Invertase can be obtained of sufficient strength to invert a 10% sucrose soln. in 2 hrs. The activity of invertase may be retained for a year and a half.

C. H. CHRISTMAN

Sucrose-salt combinations. W. D. HELDERMAN. *Arch. Suikerind.* 29, 1167-73 (1921).—As further proof of the non-existence of sucrose-salt compds. in Java molasses, H. gives the analyses of the liquid phase of the various systems examd. by him, in the form of tables and graphs. Cf. *C. A.* 15, 322, 3231.

F. W. ZERBAN

The determination of ash in sugar. GASTON H. CUADRADO. *Louisiana Planter* 67, 159(1921).—Direct incineration of the sugar is recommended as better than sulfating. Placing the crucible on a clay triangle over an asbestos sheet allows very gentle elimination of moisture and prevents excessive swelling. Carbonaceous particles resisting burning should be extd. with distd. water and then incinerated. C. H. CHRISTMAN

The determination of reducing sugars in lead-preserved cane juice. JOSEPH B. HARRIS. *J. Ind. Eng. Chem.* 13, 925-6(1921); *Louisiana Planter* 67, 269-70(1921).—The use of 20 g. dry basic Pb acetate per l. of juice gave the best preservation. Detn. of reducing sugars was made upon the original juice and after deleading. The Meissl and Hiller method for reducing sugars was used. The reagents for deleading were dry Na oxalate, NaCl, NaHCO₃, C₂H₅O₄, H₂PO₄ and AcOH. The use of alk. and neutral salts gave results which were too low. The use of NaHCO₃ gave results within the limit of accuracy, but some results were very erratic. The addition of C₂H₅O₄ gave satisfactory values and no inversion of sucrose was noted. H₂PO₄ and AcOH were less dependable. The addition of the deleading agent must be made before filtering off the Pb ppt.

C. H. CHRISTMAN

Bacteria in sugar-cane products. M. B. CHURCH. Bureau of Chemistry. *Sugar* 23, 413-4, 491-2(1921).—Bacteria and molds are to be found in mill juice. Liming and sulfating sterilize the juice. Though the massecuite is sterile, it soon becomes contaminated in the mixers and centrifugal. Exposure of agar plates near centrifugals show the presence of molds and bacteria in large numbers. Drafts facilitate the inoculation of the massecuite by molds. Wash water should be free from bacteria. Molasses contains more bacteria and molds than the wash water. Sugar in the centrifugal showed 900 bacteria per g. while the same sugar in the screw conveyor showed 3900 bacteria. An artificial magma was inoculated with spores of molds, yeast and bacteria. The sepn. of the crystals in a centrifugal with and without the use of superheated steam followed. Steaming reduced the molds in the sugar 90% and the molds by 40% and the bacteria by 33% in the molasses.

C. H. CHRISTMAN

The effect of some decolorizing carbons upon the color and colloids of cane juice. JOSEPH F. BREWSTER AND WILLIAM G. RAINES, JR. *J. Ind. Eng. Chem.* 13, 921-3 (1921).—Comparative tests were made on the efficiency of the sulfur-lime process and of the kieselguhr-carbon process (*C. A.* 14, 2868), both used on a small factory scale, in removing colloids and color from cane juice. Four different carbons were tried. It was found that kieselguhr alone takes out more colloids than the SO₂-CaO process, and that decolorizing C reduces the colloids still further. The amt. of colloids and color removed varied not only with the C used, but also for the same C, owing probably to

differences in the quantities present in the raw juice and in the pressure used in milling. The molasses produced by the kieselguhr-C process was found to contain a sediment consisting largely of SiO_2 , Fe_2O_3 , Al_2O_3 , and CaO ; P_2O_5 , MgO and CuO were also detected; the compn. is similar to that of settling in sirups made by the sulfitation process. In some lab. expts. only one of the carbons was found to be still fairly efficient on being used a second time at the rate of 1% by wt. A third use of any of the carbons proved impracticable, as regards both decolorization and speed of filtration.

F. W. ZERBAN

Something about sugar refining. GEORGE M. ROLPH. *Sugar* 23, 419-20 (1921).—90° sugar is received in hags, dumped into a large bin and the bags are washed free from sugar. The syrup thus obtained is mixed with the raw sugar to form a magma. When sepd. from the sugar crystals through the use of centrifugals, this syrup removes the greater part of the impurities. The washed sugar is melted with sweet water from the filters to give uniform density and purity. The melted sugar is treated with kieselguhr, at the rate of 23 lbs. per ton of raw sugar melted, and lime and then filtered in Sweetland presses. The clear liquors are passed over char filters at the rate of 1300 gal. per hr. and are in contact with the charcoal for 6½ hrs. A filter is operated for 16 hrs. and handles 20,000 gal. of liquor. The decolorized liquor is concd. *in vacuo* and crystd. The crystals are removed in centrifugals and sent through the granulators.

C. H. CHRISTMAN

Douglas-fir sugar. J. DAVIDSON. Univ. British Columbia, *Canadian Field Naturalist* 33, 6-9 (1919).—In some years Douglas-fir trees become coated with sugar, which may be of value as a food, although its appearance can not be relied upon annually. It is not produced by insects but is an exudation from the needles of the trees, wherever these grow under a dry climate on east or north facing slopes. Its development is due to a delicate balance of conditions, and may be prevented by wet weather, and it does not appear where the trees grow in moister regions or where they are too much exposed to the sun. Analyses of samples collected 3 years apart gave 23.3 and 24.86% reducing sugars, resp. The presence of *melezitose* in the material has been shown by Hudson and Sherwood (*C. A.* 12, 2348).

E. T. WHERRY

Dry substance in molasses, sirups and juices by the Spencer electric oven. GEORGE P. MEADE. *J. Ind. Eng. Chem.* 13, 924-5 (1921).—A number of moisture detns. were made with the aid of this app. (*C. A.* 15, 454), to ascertain the conditions under which accurate results are obtained. By absorbing solns. of known wts. of sugar, and of invert sugar and salt, and heating for 20 min. at 110° in a rapid current of air, the total solids found agreed with those taken within less than 0.3%. Thin solns., like cane juice, are completely dried within 10 min. Molasses, sirups, and honey must first be dild. with an equal wt. of water, and must not be heated longer than 20 min. A very strong current of air must be drawn through the oven during the drying period.

F. W. ZERBAN

Collection of bagasse samples. BÖHTLINGK. *Arch. Suikerind.* 29, 1191-3 (1921).—If maceration is applied at a point very close behind the individual mill sets, a truly representative sample of bagasse can only be obtained if the maceration be cut off shortly before taking the sample; or else, if it is desired not to stop maceration entirely while samples are being collected, there may be installed a three-way stopcock connecting with a second maceration pipe at some distance, which may be used during such interruptions.

F. W. ZERBAN

A new heating and evaporating system. SAILLARD. *Circ. hebdom. synd. fabr. sucre, Supplement, June 5, 1921; Z. Ver. deut. Zuckerind.* 71, 586-7 (1921).—This system, patented by Vincent, consists of (A) an open or closed boiler in which the juices are heated close to the b. p.; (B) an evacuated vessel into which the hot juice is drawn; (C) a special

app. which aspirates the steam generated in the vacuum vessel and raises it again to 100°; this steam can then be used again for heating or for driving a low-pressure turbine. The heat saved could be utilized in a salt refinery or for generating electricity. S. offers the following comment: (1) There are only 2 sugar factories in France which could take advantage of the system in connection with salt refining; the elec. energy would find buyers for only 2 months in the yr. (2) There are no sugar factories which have any use for the steam outside of the factory, unless they have a distillery or refinery connected with them. (3) Vincent does not give sufficient data for calcg. the heat losses in the juice heater or turbine; at any rate the exhaust from the turbine could not be used. (4) Vincent does not disclose the mechanism of his app. mentioned above under (C); the system of Prache and Bouillon gives good results in other industries.

F. W. ZERBAN

Steel foundry makes sugar-mill machinery (ZIMMERMAN) 9.

29—LEATHER AND GLUE

ALLEN ROGERS

Sampling of leather and its preparation for analysis. Committee report 1921. F. H. SMALL. *J. Am. Leather Chem. Assoc.* 16, 394-430(1921).—Samples for analysis are reduced to a fine condition by means of rip saws of 8-10" (23-25.4 cm.) diam. with staggered teeth and a speed of 2500-3000 r. p. m. Samples are to be placed in airtight containers immediately after prepn. Analysis includes detn. of water, fats, water-sol. ash, Epsom salt, sugars, and N. Charts accompany the tabulated results obtained by each member of the committee to show the portion of the hide represented by each sample analyzed. The number and size of samples should be as small as possible and their location such as to include parts of the hide divergent in compn. W. H. B.

The determination of available calcium oxide in lime used for unhairing hides. T. P. VITTSCH AND T. D. JARRELL. *J. Am. Leather Chem. Assoc.* 16, 438-44(1921).—A review of methods for detg. available CaO. The value of lime for unhairing hides is dependent upon its available CaO or the more sol. alkalies (NaOH and KOH) neither of which is objectionable in small quantities. The modified tannery method: a 1-g. sample, 60-mesh, is placed in a graduated 1. flask, 10 cc. of hot freshly boiled distd. water added and the flask well shaken. After slaking, small glass beads and about 950 cc. of freshly boiled distd. water at room temp. are added. The flask is stoppered and shaken 6 times for 5 min. each at 1-hr. intervals. After filling to the mark, thoroughly mixing, and settling (best overnight), 100 cc. of the clear soln. is pipeted into an Erlenmeyer flask and the available CaO detd. by titration with 0.1 *N* HCl with phenolphthalein. The modified Scaife method: 1.4 g. of a 100-mesh sample is treated with 150 cc. hot water in a 250-cc. beaker, heated carefully and then boiled for 3 min. After cooling and adding 2 drops of phenolphthalein, the soln. is titrated rapidly and with vigorous stirring with 0.1 *N* HCl until the color fades out for a second or two. The expt. is repeated in a graduated 500-cc. flask with 4.5 cc. less acid than before. The number of cc. used is "A". Any small lumps are ground up with a flat glass rod and the soln. is dild. to the mark, mixed and allowed to settle $\frac{1}{2}$ hr. 100 cc. are drawn off without filtering, and titrated with 0.5 *N* HCl; this number of cc. is "B". The % of available CaO = $(2A + 5B)$. Method I is considered more accurate and II, in skillful hands, accurate and more rapid. W. H. BOYNTON

Viscosity of gelatin solutions. CLARKS E. DAVIS, EARL T. OAKES AND HAROLD H. BROWNE. *J. Am. Chem. Soc.* 43, 1526-38(1921).—Using a method based on the Ostwald viscometer and accurate to within 0.5%, the authors found that the viscosities

of bone, ossein and hide gelatins increase with age at different rates, depending upon concn. of gelatin, H-ion concn., and variety of gelatin. Max. viscosity is reached after about 24 hrs., a decrease thereafter indicating bacterial decompn. At 25° max. viscosity is exhibited at p_H 3.0 to 3.5; but viscosity is not a simple function of concn. OH ions catalyze the hydrolysis of gelatin more rapidly than do H ions. Boiling produces speedy hydrolysis.

JEROME ALEXANDER

New process for drying glue (the Otto Ruf system). ANON. *Chem.-Ztg.* 45, 771-2(1921).—The patented feature consists in making an air emulsion of the glue or gelatin soln. in a special emulsifier provided with a jacket for heating or cooling. Rapidly revolving beaters working against fixed ones produce the form, which flows through a pipe to a slowly turning drying roll. An adjustable doctor regulates the thickness of the emulsion layer on the roll, and a scraping knife removes the dried glue in the form of a film which is automatically fed to a grinder, whence it passes into bags or barrels. The drying roll has a close jacket through which is forced a current of air that removes the vapors. It is claimed that 90 lb. of steam will evap. 100 lb. of water and that a relatively large output is obtained at low cost.

JEROME ALEXANDER

Impregnating leather, cloth or similar materials with cellulose nitrates. J. J. BYERS. U. S. 1,388,169, Aug. 23. A soln. formed of nitrocellulose, nonoxidizing oil and volatile solvents is used for impregnating leather, textile fabrics or other porous materials.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Fifty years of German rubber science. FRITZ GROSSMANN. *Chem.-Ztg.* 45, 973-4(1921).

E. H.

Note on the history of synthetic rubber. I. KONDAKOV. Lille. *Rev. prod. chim.* 24, 561-3(1921).—Polemical against Harries (Autopolymerization of butadiene in the cold), C. A. 15, 3227. K. claims priority for the discovery of the mechanism of the cold polymerization of butadiene into compds. resembling rubber. A. P.-C.

Process of vulcanization of rubber by hydrogen sulfide and sulfur dioxide. ANDRE DUBOSC. *Bull. soc. ind. Rouen* 49, 63-5(1921); cf. C. A. 15, 1089, 1421.—Further refutation by D. of Peachey's invention. It is reiterated that Peachey's process is in reality a com. application of the principle enunciated by D. some years previously (C. A. 9, 1858).

C. C. DAVIS

